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CONTENTS

E. MATHIAS, C. A. CROMMELIN, H. KAMERLINGH ONNES and J. C. SWALLOW: "The rectilinear diameter of helium", p. 526.

J. CLAY: "Helium in earth-gases of the petrol sources". (Communicated by Prof. H. KAMERLINGH ONNES), p. 529.

J. CLAY: "Electric phenomena in the atmosphere". (Communicated by Prof. H. KAMERLINGH ONNES), p. 531.

H. R. WOLTJER: "Magnetic researches. XXVII. Magnetic properties of some paramagnetic chlorides at low temperatures. (Communicated by Prof. W. J. DE HAAS), p. 536.

H. R. WOLTJER and H. KAMERLINGH ONNES: "Further experiments with liquid helium. Z. Magnetic researches. XXVIII. Magnetisation of anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ at very low temperatures", p. 544.

G. SCHAAKE: "Representation of the Pairs of Points that are Associated relative to a Conic, on the Points of Space". (Second communication). (Communicated by Prof. JAN DE VRIES), p. 550.

G. SCHAAKE: "An Involution in the Rays of Space through which a Quadratic Scroll is Associated to a Plane Pencil". (Communicated by Prof. JAN DE VRIES), p. 556.

F. A. H. SCHREINEMAKERS: "Equilibria in systems in which phases, separated by a semi-permeable membrane" X, p. 564.

ERNST COHEN and H. L. BREDÉE: "The fictitious heats of solution of enantiotropic modifications at their transition point", p. 573.

EUG. DUBOIS: "The Palaeothermal Problem in the Light of the Giant and Dwarf Theory of Stellar Evolution", p. 587.

A. J. KLUYVER and H. J. L. DONKER: "The catalytic transference of hydrogen as the basis of the chemistry of dissimilation processes". (Communicated by Prof. G. VAN ITERSON Jr.), p. 605.

J. VAN DER HOEVE: "On Enlargement of the "Optic Foramen", p. 619.

Physics. — "*The rectilinear diameter of helium*" [1]. By E. MATHIAS, C. A. CROMMELIN, H. KAMERLINGH ONNES and J. C. SWALLOW. (Communication from the Physical Laboratory at Leiden).

(Communicated at the meeting of March 28, 1925).

§ 1. Our investigatons of the density-curve and the diameter of helium cover the temperature range between the critical point (5°. 19 K.) and the boiling-point (4°.22 K.) of this substance; they are the continuation of our determinations concerning the density-curves and diameters of oxygen, argon, nitrogen, hydrogen and neon [2].

§ 2. We have made use of a helium cryostat in which the helium boils under a pressure greater than atmospheric. In this way the critical point can be reached without danger to the apparatus, as the critical pressure only amounts to 2.26 atm.

The temperature was determined by means of vapour-tension measurements, while of course the pressure measurements gave no difficulties at all. The helium originated from the evaporation of liquid helium and so could be considered perfectly pure.

We have adopted for the weight of a litre of gaseous helium under normal conditions the value of RAMSAY and TRAVERS, 0.1787 grammes.

§ 3. In the following table we have given the numbers obtained for the densities $\varrho_{liq.}$ and $\varrho_{vap.}$ of the liquid and of the saturated vapour respectively in grammes per cM^3. at the same temperature θ (thermodynamic scale) and for the ordinates of the diameter $y = \frac{\varrho_{liq.} + \varrho_{vap.}}{2}$; we have included some liquid densities at and below the boiling-point determined by Dr. BOKS and one of us (H. K. O.) [3]; we have calculated the vapour densities by means of the isotherms at low temperatures, also determined by Dr. BOKS and one of us [3]).

In calculating the linear formula of the diameter by the method of least squares we have neglected the measurements at the temperatures

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[1] A detailed communication about this subject will shortly be published as N^0. 172*b* of the Comm. from the Phys. Lab. Leiden.

[2] These Proceedings Febr. 1911, Oct., Dec. 1912, Jan. 1913; Vol. **17** p. 953, Vol. **23** p. 1175. Ann. de physique (9) 19 (1923), p. 231.

[3] 4th Int. Congress of Refrigeration. Travaux de la première commission internationale p. 215. Comm. Leiden N^0. 170*b*. Thesis for the doctorate J. D. A. BOKS. Leiden, July 1924.

θ (Celsius scale in Kelvin degrees)	T (Kelvin scale in Kelv. degrees)	$\rho_{liq.}$	$\rho_{vap.}$	$y(W)$	$y(R)$	O—C abs.	O—C in %
—268°.38	4.71	0.1139 1)	0.02699 1)	0.0704^5	0.0701^5	+0.0003	+0.43
268°.50	4.59	1165	2389	702	703^5	— 1^5	—0.21
268°.86	4.23	1253	1637	708^5	710	— 1^5	—0.21
268°.87	4.22	1255 2)	1618 3)	708^5	710	— 1^5	—0.21
269°.19	3.90	1311	1176	714^5	715^5	— 1	—0.14
269°.79	3.30	1395	06435	729^5	726^5	+ 3	+0.41
270°.53	2.56	1457	02079	739	739^5	— 0^5	—0.07
270°.72	2.37	1466	01368	740			
270°.79	2.30	1469	01159	740^5			

2°.30 and 2°.37 K. The curve of the liquid densities shows a maximum at about 2°.30 K., so that the linear relation no longer applies to the continuation of the diameter.

The formula of the diameter becomes:

$$y = -0.40263 - 0.0017616\,\theta.$$

The inclination coefficient of the diameter is thus:

$$a = 0{,}0017616.$$

The above mentioned formula gives for the critical density at the critical temperature —267°.90 C. (5°.19 K.).

$$\varrho_k = 0.06930.$$

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1) Values experimentically determined (MATHIAS, CROMMELIN, ONNES, SWALLOW).

2) Values experimentically determined (ONNES and BOKS); these observations were relative, as the normal volume left something to be desired. They have been corrected therefore by means of the numbers under 1) (of which the normal volume was determined much more accurately).

3) Values calculated from the formula

$$\varrho_{vap} = \frac{kp}{A_A\,\{1 + B^{(p)}\,p + C^{(p)}\,p^2\}}$$

k = weight in gr. of 1 cm^3 of helium at normal circumstances.

p = pressure in international atmospheres.

$B^{(p)}$ and $C^{(p)}$ are the coefficients in the series

$$pv_A = A_A\,\{1 + B^{(p)}\,p + C^{(p)}\,p^2 + \ldots\ldots\}$$

The values of $B^{(p)}$ and $C^{(p)}$ have been calculated from the isotherms of helium at helium temperatures of ONNES and BOKS l.c.

The critical coefficient becomes:

$$K_4 = \frac{R\,T_k\,\varrho_k}{p_k} = 3.270$$

a value almost equal to that of hydrogen (3.276).

§ 4. The deviations of the rectilinear diameter are small (though greater than for hydrogen and neon). So we can conclude that helium obeys the law of the rectilinear diameter in the same way as the other substances investigated. The deviations all being smaller than $^1/_2\,^0/_0$, are somewhat too great to be considered as experimental errors; besides, the systematical character of these deviations is indisputable. This systematical character is of the same sort as that of argon, neon and nitrogen, that is convex to the temperature-axis at low temperatures and concave at higher temperatures.

This investigation has been made with the aid of financial help of the Caisse des Recherches out of which the Académie des Sciences at Paris placed a subvention at our disposal. For this subvention we return our cordial thanks.

Physics. — *"Helium in earth-gases of the petrol sources"*. By Dr. J. CLAY. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of March 28, 1925).

Both from a geological and a technical point of view it is of importance to know whether helium occurs in the earth gases of the petrol sources in India. In other places namely sources have been found containing so much helium that the balloons of large airships can be filled with it.

The Bat. Petrol. Company was so kind to take carefully considerable quantities of gases from their sources and to present these to the physical laboratory of Bandoeng for our researches.

Some samples were first freed from their and expediated in shut drums of 5 L. but most samples were transported in large drums of 100 L. or in steel high pressure tubes.

In all cylinders care was taken for a sufficient overpressure (shut by water) so that no air could enter.

In order to investigate spectroscopically the presence of helium in the gas, we had to be sure that it did not contain traces of hydrogen, as the hydrogen spectrum can render that of helium imperceptible. This was the greatest difficulty with most samples.

The absorption of the hydrogen by palladium proved to be insufficient. As the only method to get rid of the hydrogen we mixed the gas with a considerably surplus of oxygen and then burned the hydrogen in a Drehschmidt capillar tube.

Thereto we mixed the gas with five times its volume of oxygen and made it flow through the capillar so often till no longer a decrease of volume was observed.

Then the remaining oxygen was taken away by pyrogallol solution, while the carbonic acid was absorbed by a potassium solution. Finally the remaining gas was led into a reservoir of known volume, while the pressure could be read. Then the gas was let into that part of the apparatus where at the temperature of liquid air it comes in contact with cocosnutcoal. Here all gases were absorbed except helium. Though at atmospheric pressure the absorption of helium at the temperature of liquid air amounts to 20 %, it may be neglected at the low pressure we finally had in the apparatus (surely below 1 mm. mercury), the absorption being proportional to the gaseous pressure. The latter could be measured in a MAC LEOD vacuummeter. In order to treat a large quantity of gas the reservoir was generally filled 5 times, while the new quantities were introduced while it contained still the gas left when the coal is regenerated by heating and evacuation by the air pump.

The finally obtained gas rest was then collected in a fresh tube with coal and brought at the temperature of liquid air.

Each time the nature of the gas was examined in a spectral tube by means of a HILGER spectrograph (of constant deviation) the spectrum being compared with that of pure helium. In this way helium was stated in the samples from

Ledokput	158	Tjepoe	Java
Ledokput	135	„	„
Banjoeasin	17	„	„
Djerigi put	15	„	„
Tg. Lontar	I, V, VI	Pladjoe	Sumatra.

The following gases contain small traces of helium, probably still less than the given percentages. The latter reserve must be made as very small traces of other gases might be present, though these have not been stated spectroscopically. Always the mercury spectrum was visible. The pressure of the mercury vapour however is not measured in the MAC LEOD vacuummeter:

Gaboes	0,0014 %	Tjepoe	Java
Semanggi 66.	0,0013 %	„	„
Semanggi 62.	0,0017 %	„	„
Banjoebang 15.	0,0020 %	„	„
Nglabo	0,0033 %	„	„
Zuid-Perlak	0,0030 %	Pankalanbrandan	Sumatra
P. Soesoe	0,0015 %	„	„
Papa Drien	0,0006 %	„	„

Bosscha Laboratory Techn. Highschool
July 1924. *Bandoeng (Java).*

Physics. — "*Electric phenomena in the atmosphere*". By Dr. J. CLAY. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicatcd at the meeting of March 28, 1925).

§ 1. All investigators of the electric phenomena in the atmosphere agree that in the first place we want observations at different places and of long duration, as we have not yet a sufficient insight in these phenomena.

It seemed to me of importance to make observations at a place, where the meteorological states vary more regularly than in the temperate regions where until now most data have been collected. Especially I intended to investigate the different parts of the phenoma at the same time.

The different phenomena to be investigated are:

1st. the value and the variation of the electric charge of the earth, which can be determined by the potential gradient,

2nd. the charge and the conductibility of the atmosphere and their variation,

3rd. the percentage of emanation in the air and in the earth,

4th. the penetrating radiation of the earth and of cosmic origin. These two latter phenomena cause the ionisation of the air,

5th. the electric charge of the rain.

These are the electric phenomena that have been put on the preliminary working programme of the Bandoeng laboratory.

Since a few months we have started a photographic registration of the potential gradient, as well as also determinations of conductibility and number of ions, while preliminary experiments are made on the percentage of emanation, on the penetrating rays and on the electric charge of the rain.

§ 2. As to the potential gradient, this is determined by means of a ionium collector projecting 75 cm. above the *top* of the physical institute while the ridge itself is earthed by means of two thick iron wires.

The collector is isolated on amber, which has been dried by means of sodium brought into its immediate neigbourhood in a glass tube.

The connecting wire of the electrometer is lead through a glass tube; through the roof and the ceiling, it directly goes to the electrometer.

The electrometer has been made in the Bandoeng laboratory; it is a binant electrometer of the CURIE type but it has a fixed and a rotating cylinder instead of a box with a needle. Further it has the advantage that by means of a mirror the rotation of the cylinder can be registrated, while quite independently a second mirror makes continuous direct reading on a fixed scale possible.

In order to fix the absolute value we compared during several days the obtained values of the potential gradient with those found at different places of the open land belonging to the Technical Highschool. The reduction factor proved to be 2,2. This means that the value of the potential at the roof has to be divided by this factor.

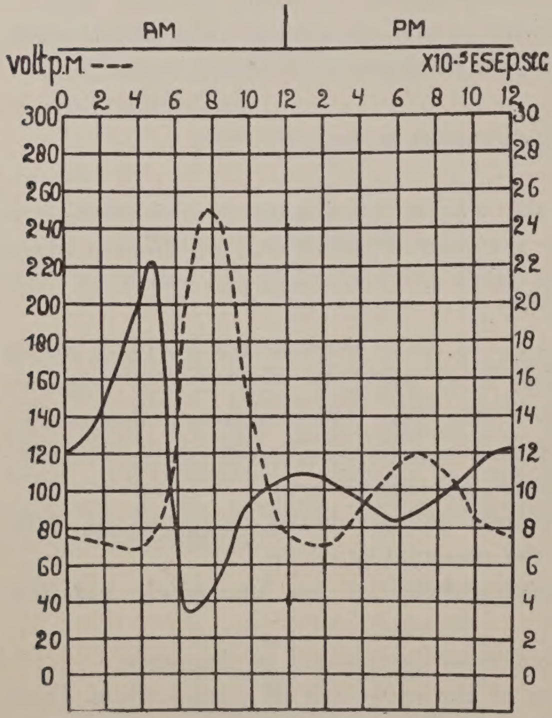

Fig. 1. Potential gradient and conductivity of the air.

The dotted line in this figure indicates the value of the potential gradient while the value of the conductivity is given by the uninterrupted line.

From fig. 1 we see the most striking feature of the diurnal variation of the potential gradient. It is a highly developed maximum at $8^{1}/_{2}$ a.m. local time. This maximum is about 2 to 2,5 times as high as the mean value over the day and about 4 to 5 times as great as the immediately preceding and following values.

The mean value is about 90 volt, the maximal value 250 volt pro meter.

A second much smaller maximum is found at $8^{1}/_{2}$ p.m., while the weak minimum lies of at about 4 a.m.

On the whole the variation curve resembles very much that found by KÄHLER in July at Potsdam. The only difference is that at Bandoeng the a.m. maximum is much stronger developed.

The time of this maximum does *not* agree with the results of the investigations of S. J. MAUCHLY [1]), who compares the data collected on the cruisades of the „Carnegie" through different oceans and also those found at the coast stations. He comes to the conclusion that the diurnal variation has a maximum which occurs for all stations at about the same time viz. at about 17 G.M.T. For Bandoeng this would be at about midnight local time.

The theory of EBERT explains the negative charge of the earth.

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[1]) S. J. MAUCHLY. On the diurnal variation of the potential gradient. Terr. Magn. a. Atm. Electricity Vol. 28, p. 61, 1923.

According to it the high potential gradients should occur *after* the falling of the barometer, which does not agree at all with the Bandoeng results.

How to explain then the high maximum?

To this purpose we shall want in the first place other simultaneous data f.i. on the conductibility and the number of ions.

We have tried whether the great variation of the gradient is connected with the change of the degree of moisture. During the time of the measurements (dry season) the amount of water vapour varied from 6—9 in the morning on an average from 11.5 to 14.5 that is by 25 $^0/_0$. This might reduce the mobility of the ions somewhat, but not enough to explain the change of the conductibility.

In the meantime the relative degree of moisture fell from 90$^0/_0$ to 50$^0/_0$.

§ 3. Finally we may remind that recently from different sides a connexion has been sought between the value of the potential gradient and the solar activity. HUNTINGTON's "Earth and Sun" (published in the beginning of 1924) gives a detailed account of these investigations. He wants to prove that it is of great importance to investigate the variation of the gradient in order to have a measure for the solar activity, which again strongly influences all meteorological factors.

March 1924 L. A. BAUER [1]) published a calculation according to which during the two last sun spot periods 1901—1923 a variation of the sun spot number by 100 corresponds to an increase of 20 to 35 $^0/_0$ of the mean potential gradient. For the correlation coefficient he gives 0.75, which suggests an intimate connexion.

§ 4. The electric state of the atmosphere was determined by two different methods. First by measuring the dispersion of the electricity by a conductor of 14,4 cm. capacity connected with a bifilar Wulf electrometer. According to theoretical considerations of SWANN [2]) the form of the electrically charged body is of no importance, while the charge, emitted by a body with charge Q is given by $4\pi Q n e v$, where v denotes the mobility of the electric charges, e the charge and n the number of charges pro cm^3. When we write for the capacity of the conductor as far as it is surrounded by air C, for the capacity of conductor and electrometer together C_1, for the potential V, we have

$$-C_1 \frac{dV}{dt} = 4\pi C V n e v.$$

or integrated

$$C_1 \, lg \frac{V_1}{V_2} = 4\pi n e \, VCT,$$

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[1]) L. A. BAUER. Correlations between solar activity and atmospheric electricity. Terr. Magn. a. Atm. Electr. March 1924 p. 23.

[2]) W. F. G. SWANN. The theory of electrical dispersion into the free atmosphere. Terr. Magn. a. Atm. Electr. Vol. 19. p. 81 1914.

when V_1 is the initial potential and V_2 the potential after T seconds.

By means of this formula nev can be calculated. This quantity is called the conductibility of the air. Both for positive and negative charges it was determined during several days with intervals of a few hours, so that the diurnal variation could be found. This conductibility too was proved to vary strongly.

From fig. 1 we see, that at four o'clock in the night a strongly defined maximum occurs, which is shortly followed (at about half past six) by a minimum. Generally the potential gradient has a maximum, when the conductibility shows a minimum, as might have been expected. It is of importance to find out which of the two is primary and perhaps the cause of the other. It is most suggestive that the variation of the potential gradient is caused by that of the conductibility.

It is interesting to investigate which is the cause of the variation of the conductibility as we have two factors that may undergo a change viz. the number of charges pro unit of volume and the mobility.

To this purpose it is desirable to determine at the same time both conductibility of the air and the number of ions pro cm^3., which may be done by the method of EBERT. We took a cylindrical tube of 1 m length and 15 cm. diameter in which an isolated tube is suspended.

The air is pumped through this tube, which is kept at a potential of 200—300 volt, so that *all* charges of the same sign are driven towards the rod, which is connected with a binant electrometer. The capacity of rod and electrometer as a whole is 75 cm. The sensibility of the electrometer is 120 mm. pro volt. Generally the charge is measured up to 200 mm. Before the natural leakage has been determined. The quantity of air pumped through the tube is sufficient to cause a charging of the electrometer to 1,66 volt in 1—2 minutes. The velocity of the air is controlled by a tested venturimeter.

In this way the charge of a definite kind of ions pro unit of volume of the air is determined directly, so that the quantity *ne* is known.

On different days the conductibility does not vary in the same way exactly as the number of ions, though these two quantities often correspond very well. So we found f. i. on one day for the ratio between the conductibilities at noon and at 8 a. m. 1,30, and for the ratio of the number of ions at the same moments 1,29.

From these data we find for the mean number of positive ions pro cm^3. 260 and for that of negative ions 220 both at noon.

Several recent researches suggest that the different variation of the mobility on different days is due to the different degree of moisture of the air. As has been found by J. J. THOMSON and stated by a recent research of NOLAN[1]) the ions are bound to small clumps of 14—36 water molecules, which give a mobility of resp. 1,87—2,24 cm. sec. pro unit of potential gradient. The above mentioned value of 260 ions gave a mean mobility of 2,4 cm., which can be explained partially by the higher temperature and the lower pressure, compared with those used by NOLAN.

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[1]) J. J. NOLAN. The constitution of gaseous ions. Physical Review July 1924 p. 16.

A better insight will not be possible before numerous other observations will have been collected.

§ 5. Further we must investigate by which ionising actions the ionisation of the air is maintained.

A few observations have been made already on the percentage of emanation of the air.

Through a second cylinder equal to the first one air was pumped during 2—3 hours, while the rod was kept at 1500 volt, so that the emanation settles down on the rod. Afterwards the loss of charge of the rod is measured. The quantity of air passed through the tube was known, while the loss of charge could be compared with that found, when a known quantity of emanation from a standard solution of RUTHERFORD was introduced into the tube. For the emanation we found in this way 3.10^{-19} Curie pro cm^3. This is a rather low value, which agrees with the small number of ions that was found.

§ 6. Incidentally the potential gradient and the conductibility were measured at some mountain tops of Java, from which then the number of ions was derived. We were struck by the exceedingly high gradient as well as by the fact, that the number of negative ions sometimes exceeded that of the positive ones.

On the Tjikoray (2824 m.) we found in October as 7 a. m. 400 volts pro meter, at noon 700 volt pro m. at 5 p. m. 800 volt pro m. Thus the variation is quite different from that on the plateau of Bandoeng.

In May we found on the Pangerango (3025 m) 350 volt at 7 a. m. gradually rising to 450 volt at 5 p. m. Both here and on the Tjikoray it was impossible to measure during the night because of the condensation of watervapour on the supporting rod by the strong heat radiation. For the number of ions pro cm^3. we found:

			+	—
October	Tjikoraj	2824 M.	347	425
May	Pangerango	3024 M.	207	365
June	Patoea	2400 M.	85	151
May	Weltevreden	10 M.	212	179
Aug.	Bandoeng	760 M.	260	220

These detached data do not yet allow many conclusions. It is only evident that generally the number of ions is small.

September 1924.

Bosscha Laboratory of the Technical Highschool. Bandoeng. Java.

Physics. — "*Magnetic researches.* XXVII. *Magnetic properties of some paramagnetic chlorides at low temperatures.*" By H. R. WOLTJER. (Communication N⁰. 173*b* from the Physical Laboratory at Leiden). (Communicated by Prof. W. J. DE HAAS.)

(Communicated at the meeting of May 30, 1925).

§ 1. *Introduction.* The strong increase at low temperatures of the specific magnetic susceptibility χ, according to the law of CURIE $\chi T = C$, had raised, as soon as further researches on this subject were undertaken (first oxygen, then powdered salts) the question whether such substances on sufficiently continued cooling would show ferromagnetism.[1]) It then soon appeared[2]), that obedience to the law of CURIE only means a special case of obedience to a more general relation $\chi(T + \Delta) = C$, Δ being an individual constant for each substance, which at first was always found to be positive. For ferromagnetic substances above the CURIE-point a similar law holds, the law of WEISS $\chi(T - \theta) = C$ deduced by him from his theory. So, as θ is ascribed to the appearance of a molecular field, Δ may be connected with a negative molecular field, as already mentioned by WEISS and FOËX in their research on the magnetisation of ferromagnetic substances above the CURIE-point.[3])

It is evident that substances with a positive Δ cannot be cooled down to the CURIE-point; moreover the later so called cryomagnetic anomaly[4]) appears. The substances with negative Δ form a different group, to which, as found by CABRERA[5]), nearly all chlorides belong. Now, a negative value of Δ is in itself not sufficient argument for expecting ferromagnetic phenomena at temperatures below $-\Delta$, e.g. one has to be prepared for the appearance of the cryomagnetic anomaly. This circumstance is left out of consideration by THEODORIDES[6]) in his conclusion that one may presume a real CURIE-point for the chlorides as their molecular field is positive. The researches of ISHIWARA [1]) showed however, that the cryomagnetic anomaly for anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ has not yet appeared in the temperature domain of liquid air. So it was important, as CABRERA had already pointed out, to investigate those substances at very low temperatures.

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[1]) H. KAMERLINGH ONNES and A. PERRIER, these Proceedings 12, p. 799; Leiden Comm. N⁰. 116.

[2]) H. KAMERLINGH ONNES and E. OOSTERHUIS, these Proceedings 15, p. 322; Leiden Comm. N⁰. 129*b*.

[3]) P. WEISS and G. FOËX, Arch. des Sc. Phys. et Nat. 31 (1911) pp. 4, 89.

[4]) H. KAMERLINGH ONNES, Rapport 3e Cons. de Phys. Solvay 1921, Leiden Comm. Suppl. N⁰. 44*a* I.

[5]) J. de Chim. Phys. 16 (1918) p. 442, cf. p. 490.

[6]) Diss. Zurich 1921, p. 83.

In 1921 KAMERLINGH ONNES [2]) was able to communicate as a preliminary result of this research that the cryomagnetic anomaly appeared indeed for these substances in the temperature region of liquid hydrogen, but at the same time other anomalies appeared in so far as the susceptibility became dependent on the field strength [3]). Since then the problem has been investigated at helium temperatures also. This research confirmed the particular shape of the magnetisation curves of $CoCl_2$ and $NiCl_2$ and pointed out more clearly how far ferromagnetism can be spoken of for $CrCl_3$. These results will be treated in a following communication. Here we deal with the measurements undertaken in order to confirm and to test the results of the preliminary investigation of the substances mentioned down to the triple point of hydrogen.

§ 2. *Materials, method etc.* Prof. VAN ITALLIE and Miss Dr. STEENHOUWER of the Pharmaceutical Laboratory have been so kind as to furnish us with pure anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$. In order to avoid hydration the substances were transferred to the experimental tubes in an atmosphere of dry CO_2. Moreover the tubes that served for the final experiments were heated for some time before being sealed off. The preliminary experiments were carried out according to the „rod-method"; as at hydrogen temperatures the succeptibility appeared to become dependent on the field strength, the final experiments were carried out by measuring the attraction experienced by a „sphere" in an inhomogeneous magnetic field. In the following we mention the results of the final series only. In this the attraction was measured by electrodynamic compensation [4]) except for $CrCl_3$ in liquid hydrogen, as here the forces became too large for this method. For the corrections to be applied we refer to a previous communication [5]). Here we mention only that the temperature determination of the liquid bath was considerably improved as compared with previous measurements, a stirrer [6]) and a resistance thermometer being used.

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[1]) T. ISHIWARA, Tôhoku Sc. Rep. 3 (1914), p. 303.

[2]) l.c. § 5*e* footnote.

[3]) If the susceptibility depends on the field strength one can only speak of cryomagnetic anomaly, if the results for a given value of the field strength are compared.

[4]) H. KAMERLINGH ONNES and A. PERRIER, these Proceedings 16, p. 689; Leiden Comm. N⁰. 139*a*.

[5]) H. R. WOLTJER, these Proceedings 26, p. 613; Leiden Comm. N⁰. 167*b*.

[6]) A. PERRIER and H. KAMERLINGH ONNES, these Proceedings 16, p. 901; Leiden Comm. N⁰. 139*d*.

§ 3. *Results and discussion.*

a. Above hydrogen temperatures,

TABLE I.
$CrCl_3$ anh.

T	$10^6 \chi$	$10^5 \chi (T-32.5)$
288°.0 K	41.0	1048
285.9	40.6	1028
285.0	40.0	1010
248.3	47.8	1031
239.2	49.3	1018
224.3	54.0	1035
211.1	56.8	1015
199.2	60.7	1013
199.1	62.2	1036
170.7	74.0	1023
153.1	85.0	1025
136.1	99.6	1032
64.2	294.7	934

For $CrCl_3$ (table I) down to the lowest ethylene temperature the relation $\chi(T-\theta)=C$ holds.

θ, determined graphically from a $^1/\chi$, T-diagram, equals 32°.5. The CURIE

TABLE II.
$CoCl_2$ anh.

T	$10^6 \chi$	$10^5 \chi (T-20)$
288°.7 K	90.8	2441
287.9	90.8	2433
249.6	105.0	2411
195.5	139.7	2452
169.7	163.3	2444
137.2	206.5	2420
77.5	421.1	2423
64.0	544.9	2396

constant then becomes 0.01025 corresponding to 17.9 magnetons. From ISHIWARA's measurements we derive: $\theta = 44^\circ.2$, $C = 0.01102$, n (number of magnetons) $= 18.53$. Usually the ion $Cr^{\cdot\cdot\cdot}$ is supposed to have 19 magnetons.[1])

For $CoCl_2$ (table II) down to liquid nitrogen the relation $\chi(T-\theta) = C$ holds.

θ, determined graphically from a $^1/\chi$, T-diagram, equals 20°. The CURIE constant then becomes 0.02432 corresponding to 24.93 magnetons. From ISHIWARA's measurements we derive: $\theta = 33^\circ$, $C = 0.02401$, $n = 24.77$.

THEODORIDES (determinations above 0° C.)[2]) gives $\theta = 47^\circ.2$, $C = 0.02426$, $n = 24.96$.

To explain by moisture the difference between THEODORIDES and us as regards θ a water content of 9 % (if additivity holds) in our salt must be supposed. As traces of moisture change the colour of $CoCl_2$ to violet and our salt was slatish blue, this explanation seems to be excluded and the difference remains as yet unexplained.

TABLE III.

$NiCl_2$ anh.

T	$10^6\,\chi$	$10^5\,\chi\,(T-67)$
291°.9 K	42.2	950
291.2	42.3	949
291.1	43.1	966
289.6	44.0	980
288.7	44.1	979
249.7	51.8	947
249.0	53.6	976
230.0	59.1	963
211.0	67.6	973
195.2	76.0	974
194.7	77.1	985
169.7	94.2	968
137.6	136.5	963
77.6	414.1	438
63.9	600.1	—

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[1]) P. WEISS, J. de Phys. et le Rad. (4) 5 (1924) p. 129.

[2]) Diss. Zürich 1921; Paris C.R. 171 (1920) p. 948; J. de Phys. et le Rad. (4) 3 (1922) p. 1.

For $NiCl_2$ (table III) down to the lowest ethylene temperature the relation $\chi(T-\theta)=C$ holds.

θ, determined graphically from a $^1/\chi$, T-diagram, equals 67°. The CURIE constant then becomes 0.00971 corresponding to 15.7 magnetons.

From ISHIWARA's measurements we derive:

above 220° K. $\theta=94°$, $C=0.00933$ $n=15.4$
below „ $\theta=70°$, $C=0.01100$ $n=16.7$.

THEODORIDES (determinations above 0° C.) gives $\theta=77°.6$, $C=0.01004$, $n=16.00$.

b. In the temperature region of liquid hydrogen, in which these three substances are below their θ-temperatures, all of them show the anomaly that the susceptibility (calculated from the attraction in the ordinary manner) becomes dependent on the field strength. At higher temperatures nothing is to be seen of this, except perhaps for $CoCl_2$ at 64°.0 K. and 5 amp. through the magnet coils, in this case however the force is very small and the result of the measurement uncertain. Table IV and figs. 1—3 show the susceptibility as a function of the field strength at different temperatures: for $CrCl_3$ not χ, but χT has been plotted, as otherwise the diagram would have become too large.

TABLE IV.

I	H_0	$10^5\chi$ $CrCl_3$			$10^5\chi$ $CoCl_2$			$10^5\chi$ $NiCl_2$		
		64°.2	20°.3	14°.6	64°.0	20°.4	14°.4	63°.9	20°.4	14°.2
5	3.3	—	416 [1]	915	49.1	152	138	—	63.1	61.3
10	6.6	—	420	712	54.5	182	168	59.3	70.3	69.6
15	9.9	29.3	387	611	54.1	200	191	60.6	73.4	74.1
20	12.9	29.4	360	540	54.3	208	204	59.7	77.3	77.0
30	17.3	29.4	321	462	54.1	217	213	60.0	81.0	81.1
45	20.2	29.6	299	413	54.9	223	—	60.1	82.6	82.7
60	21.6	29.4	288	389	54.9	225	—	60.0	83.4	83.7
70	22.2	—	282	378	—	—	—	—	—	—

The first column of table IV gives the current in the magnet coils, the second the field strength in the middle of the interferrum in kilo-gauss; at the place of the samples H is about 0.8 H_0. The hydrogen values for $CrCl_3$ are corrected for demagnetisation [2]. The

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[1] In the whole of the determinations concerning $CrCl_3$ this point is exceptional and in drawing the curve of fig. 1 it has been left out of account.

[2] H. R. WOLTJER, l.c. § 3*b*.

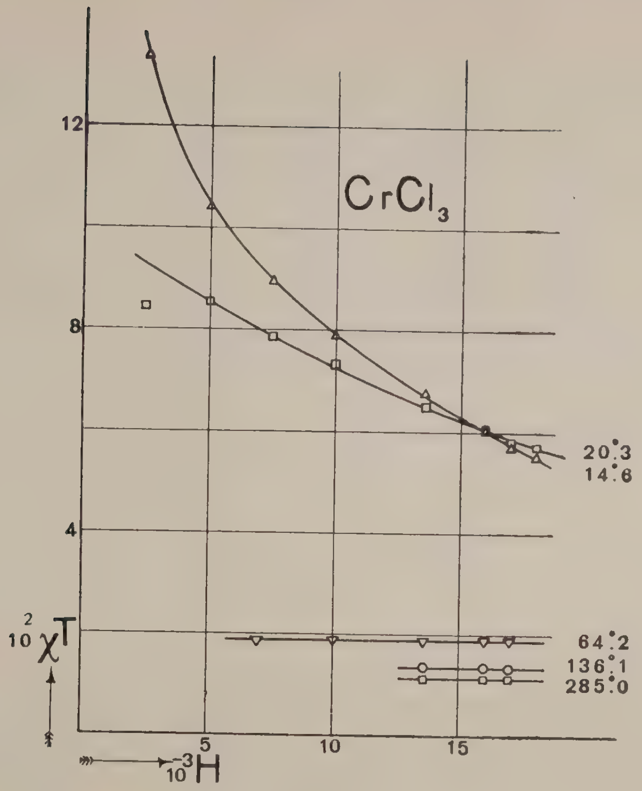
CrCl$_3$
12
8
4
$10^2 \chi T$
5
10
15
$10^{-3} H$
20°.3
14°.6
64°.2
136°.1
285°.0

Fig. 1.

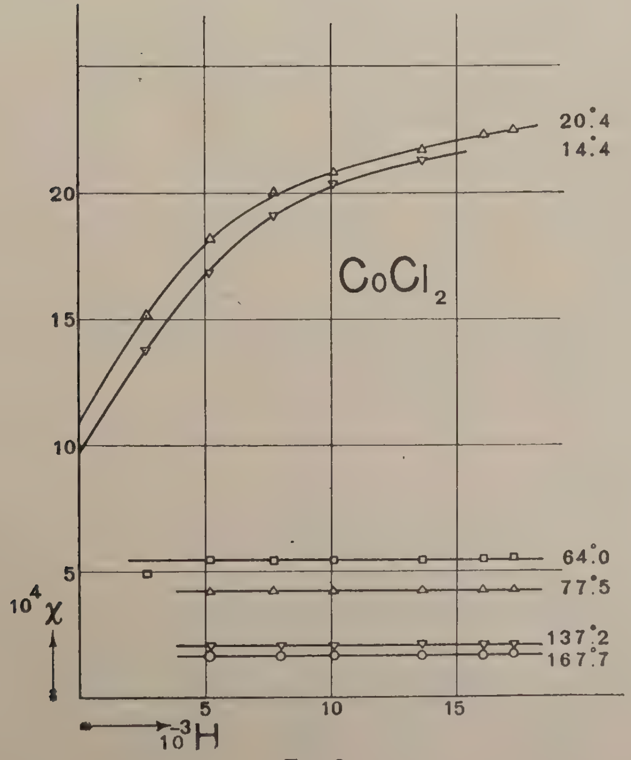
CoCl$_2$
20
15
10
5
$10^4 \chi$
5
10
15
$10^{-3} H$
20°.4
14°.4
64°.0
77°.5
137°.2
167°.7

Fig. 2.

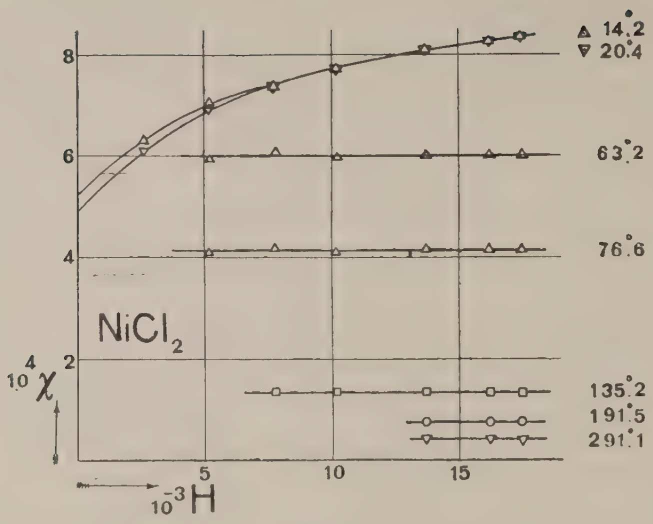

Fig. 3.

diagrams and table IV show, that for CrCl$_3$ the dependence on the field strength is opposite to that for CoCl$_2$ and NiCl$_2$ and, as corresponds to ferromagnetism, χ decreases with increasing field strength. In this sense it can be said, that CrCl$_3$ below 32°.5 K shows ferromagnetism. The magnetisation curves will be given at the same time as those for CoCl$_2$ and NiCl$_2$ in the following communication. For the latter substances the susceptibility increases with increasing field strength. This is a very uncommon feature. For CrCl$_3$ the dependence of the susceptibility on temperature is in the liquid hydrogen region still strong and, as regards the sign, normal; the susceptibility of CoCl$_2$ decreases though, slightly, with falling temperature; the susceptibility of NiCl$_2$ is independent of temperature except for weak fields in which the same phenomenon appears as for CoCl$_2$.

If the inverse initial susceptibilities are plotted as functions of temperature, the curves are, at higher temperatures, rectilinear for these three substances and in the nitrogen region convex to the T-axis, for yet lower temperatures those of CoCl$_2$ and NiCl$_2$ show a minimum.

§ 4. *Summary.*

1. For anhydrous CrCl$_3$, CoCl$_2$ and NiCl$_2$ as instances of substances with negative Δ, the susceptibility has been investigated for dependence on field strength and temperature.

2. For all of them down to the temperature region of liquid nitrogen the susceptibility is independent on the field strength. Down to the lowest ethylene temperatures all of them satisfy the relation $\chi(T-\theta) = C$ in which θ is found to be 32°.5, 20° and 67° resp.

3. In the temperature region of liquid hydrogen for all of them the

susceptibility depends on the field strength; for $CrCl_3$ it decreases, for $CoCl_2$ and $NiCl_2$ it increases with increasing field.

4. With a given field strength the susceptibility of $CrCl_3$ increases with falling temperature, for $CoCl_2$ it decreases a little, for $NiCl_2$ the initial susceptibility decreases a little.

I have pleasure in thanking Prof. KAMERLINGH ONNES very heartily for his invitation to this research and his continued interest and Mr. E. C. WIERSMA for his strong support in the final experiments and the calculation of their results.

Physics. — "*Further experiments with liquid helium. Z. Magnetic researches.* XXVIII. *Magnetisation of anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ at very low temperatures.*" By H. R. WOLTJER and H. KAMERLINGH ONNES.

(Communicated at the meeting of May 30, 1925).

§ 1. *Introduction.* In the preceding communication the magnetic anomalies shown by anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ at the temperatures of liquid hydrogen have been pointed out. It seemed to be important to extend this research to the very low temperatures obtainable with liquid helium. The following questions came to the foreground: as regards $CrCl_3$ whether the initial susceptibility would increase with decreasing temperature as strongly as in the liquid hydrogen region and whether in strong fields saturation phenomena would appear; for the other substances whether the decrease of the susceptibility with decreasing temperature that seemed to be indicated by the measurements in liquid hydrogen would be continued.

§ 2. *Method.* With the same samples to which the preceding communication refers, the magnetisation was determined from the attraction, exerted on a small quantity of the substance in an inhomogeneous magnetic field following exactly the method described in full in connection with the investigation of gadoliniumsulphate [1]).

§ 3. *Results.* For $CrCl_3$ two series of measurements in helium have been carried out and three in liquid hydrogen; for each of both other substances one series in liquid helium followed in each case by a measurement in liquid hydrogen.

It seems superfluous to give here all the figures concerning $CrCl_3$. In table I we give part of the series of 12 and 15 July 1922. These observations have been plotted in fig. 1. The curves in that diagram have been obtained by smoothing the *whole* observational material. This smoothing was performed thus: with the aid of the preliminary isotherms the curves $H =$ constant have been drawn in a σ, T-diagram (σ is the specific magnetisation, H the field strength after correction for demagnetisation) (fig. 2) and from this the final σ, H-diagram has been traced.

In table II are given the forces (in grammes) exerted on the samples of $CoCl_2$ and $NiCl_2$ (resp. 0.2990 and 0.2515g.) at different temperatures

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[1]) These Proc. **26**, p. 614; Leiden Comm. N⁰. 167*b*.

TABLE I. $CrCl_3$

T 20°.3 K		14°.6		4°.23		2°.36		1°.23	
H	σ	H	σ	H	σ	H	σ	H	σ
2.6 Kg.	11.5	2.5	25.2	2.3	35.2	2.3	36.0	2.3	36.3
5.1	22.5	5.0	38.2	4.8	47.3	4.8	48.6	4.8	49.4
7.7	31.1	7.5	49.1	7.4	57.3	7.4	58.6	—	—
10.1	38.3	9.9	57.4	9.8	66.5	9.8	66.9	9.8	67.2
13.7	45.4	13.5	65.3	13.3	77.1	13.3	78.0	13.3	78.8
16.3	49.4	16.0	68.2	15.9	83.0	15.9	84.2	15.9	85.1
17.5	51.7	17.3	69.9	17.1	86.3	—	—	17.1	88.5
18.1	52.7	17.9	70.6	17.7	88.0	17.7	89.5	—	—

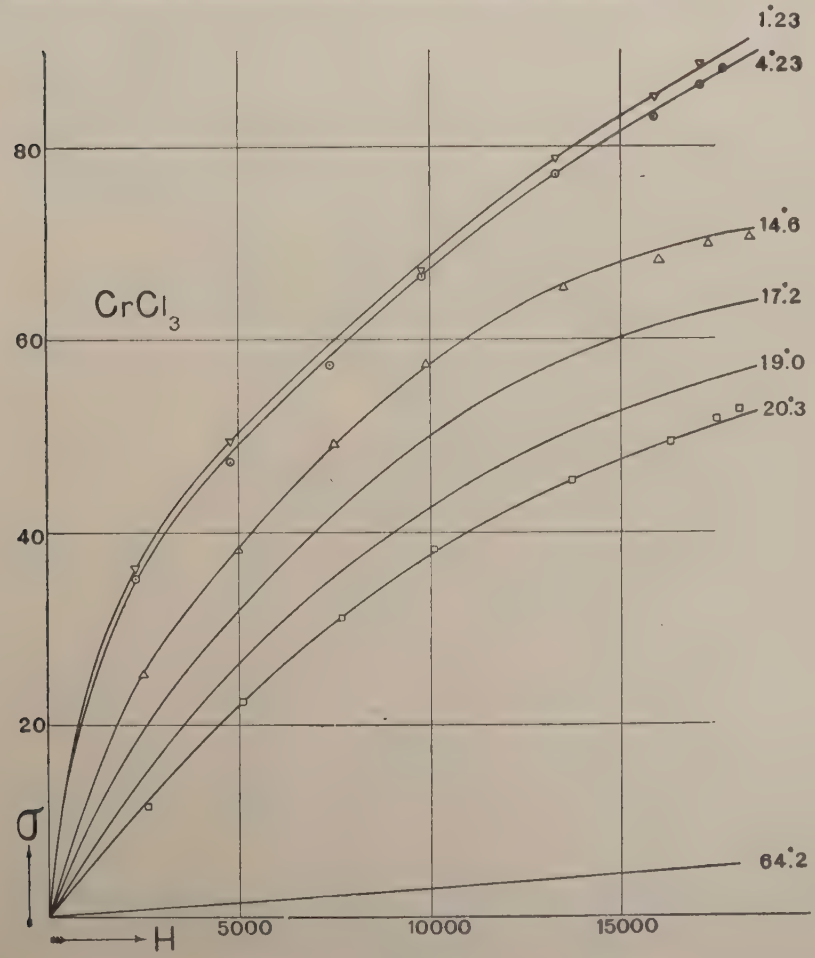

Fig. 1.

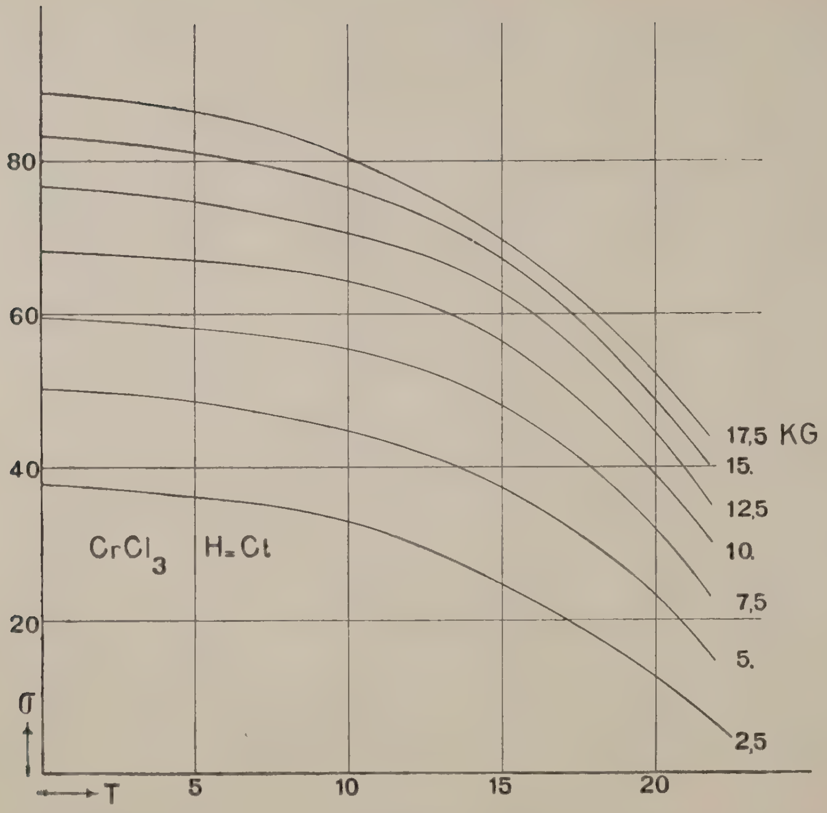

Fig. 2.

TABLE II.

I	3	4	5	10	15	20	30	45	60	70
$CoCl_2$										
20°.4 *K*	—	—	0.9	3.9	9.9	17.9	31.9	41.9	45.4	—
14.0	—	—	0.8	3.8	9.6	17.6	31.6	41.6	45.2	46.8
4.2	—	—	0.8	3.7	9.5	17.7	31.8	41.8	45.4	47.1
2.31	—	0.4	0.7	3.7	9.5	17.7	31.7	41.8	45.4	47.1
1.48	—	—	—	—	—	—	32.2	—	45.9	—
$NiCl_2$										
20.4	—	—	0.3	1.3	3.0	5.4	9.6	12.5	13.8	—
14.6	—	—	0.3	1.3	3.0	5.4	9.7	12.5	13.8	—
4.22	—	—	0.3	1.2	3.0	5.3	9.5	12.6	13.7	14.3
2.30	0.11	0.18	0.3	1.2	3.0	5.2	9.6	12.5	13.8	14.3
1.48	—	—	—	—	2.9	—	—	—	13.8	14.3

and different currents in the magnetcoils. It shows that the change of the susceptibility is very small for $CoCl_2$ and entirely out of the experimental accuracy for $NiCl_2$. The magnetisation being so slightly dependent on temperature, in table III and in figs. 3 and 4 only one magnetic isotherm is given, that for 2.°3 K. [1]).

TABLE III, $T = 2^\circ.3\ K$.

$NiCl_2$		$CoCl_2$	
H	σ	H	σ
1.6	1.1	—	—
2.2	1.3	2.2	2.6
2.7	1.6	2.7	3.5
5.2	3.6	5.2	9.1
7.7	5.7	7.7	15.8
10.2	7.9	10.1	22.5
13.7	11.3	13.6	31.3
16.2	13.6	16.1	38.0
17.4	14.9	17.3	41.2
18.0	15.6	17.9	43.1

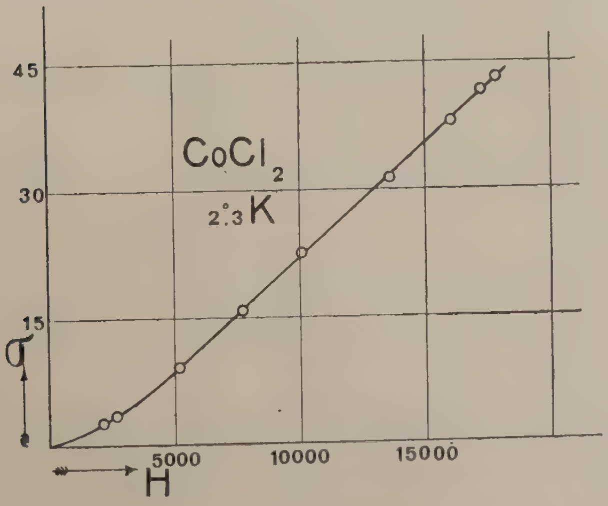

Fig. 3.

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[1]) If σ over H is taken, values for χ are found slightly different from those given in table IV of the preceding communication for $CoCl_2$ and $NiCl_2$ at 14°.2 K, even if the circumstance is taken into account, that in table III of the present communication corrections

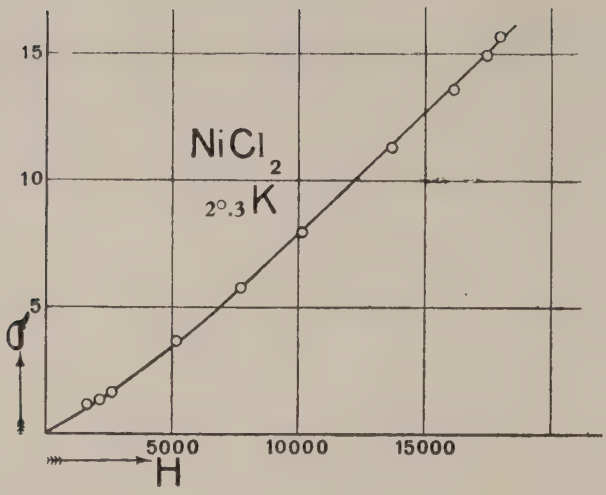

Fig. 4.

§ 4. *Discussion*. The magnetisation curves show some resemblance to those found by WEISS and FORRER [1]) for nickel in the neighbourhood of the CURIE-point, but there are also striking differences: there is no question of saturation magnetisation and the slope of the isotherm for large fields is at helium temperatures even greater than at hydrogen temperatures [2]). WEISS's theory of ferromagnetism does not seem to be applicable here. The highest specific magnetisation attained by us is 89.5 e. m. C.G.S. corresponding to 12.6 magnetons, and the saturation would correspond to 18 magnetons. Neither for $CrCl_3$ nor for the other chlorides have we found hysteresis or residual magnetism.

For $CoCl_2$ and $NiCl_2$ the magnetisation curves are for smaller fields convex to the *H*-axis, for larger ones nearly linear; the susceptibility approaches asymptotically a limit for large fields. Formally, this feature may be explained thus: the magnetisation may be considered to be a result of two components, one proportional to the field strength (in the diagram it would be represented as a straight line through the origin

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for the demagnetisation are applied. Nearly as large differences are found, if, not the calculated susceptibilities, but the values of the attraction at hydrogen temperatures found here are compared with those on which the χ-values of table IV on the preceding communication are based. The present observations have been made by means of a different apparatus and on another occasion to those of the preceding paper. The latter are no doubt more accurate, but the former are better comparable with the observations in liquid helium, since they are taken within a small interval of time, using the same method and the same apparatus. As regards $NiCl_2$ the differences remain nearly within the accuracy of the experiments (about 2%), for $CoCl_2$ they are larger (above 4%) and not yet quite explained.

[1]) Paris C.R. 178, p. 1046.

[2]) This remark only holds if the large magnetisation of the $CrCl_3$ does not influence the distribution of the lines of force and the calibration of the large magnet remains valid.

parallel to the straight part of the curve); and a second in the opposite direction to the field, which develops under influence of the field from zero to a maximum amount. However it seems difficult to see the physical meaning of this last component. As regards $CrCl_3$ the measurements do not favour the conclusion that there is a limit to the susceptibility; there seems to be no reason for replacing the last parts of the curves for 1°.23 and 4°.23 K in fig. 1 by straight lines. If there was a limit, one could perhaps think of a superposition of paramagnetism and ferromagnetism, as recently found by PESCHARD [1]).

For $CrCl_3$ it seems important to investigate the magneto-caloric effect in order to ascertain whether there is yet a spontaneous magnetisation notwithstanding the absence of saturation phenomena [2]).

§ 5. *Summary.*

1. For anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ the magnetisationcurves have been determined at the temperatures of liquid hydrogen and helium, at which temperatures these substances are below their "CURIE-temperature" [3]).

2. $CrCl_3$ shows ferromagnetism in so far as the susceptibility decreases with increasing field strength; saturation spontaneous magnetisation, or hysteresis has not been found.

3. $NiCl_2$ and $CoCl_2$ show an unusual type of magnetisationcurve, first convex to the *H*-axis, then linear for higher fields. At low temperatures the law connecting magnetisation and field strength seems to approach asymptotically to a definite form (different for $CrCl_3$ and for $CoCl_2$ and $NiCl_2$) and so to become independent of temperature; for $CoCl_2$ and $NiCl_2$ this form has been reached nearly at hydrogen temperature; for $CrCl_3$ there is only a small change in magnetisation on cooling from 4°.23 to 1°.23 K.

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[1]) Paris C.R. 180 (1925) p. 1836.

[2]) The lines $\tau = ct$ in a H, T-diagram from which, as shown by WEISS and FORRER for nickel, the spontaneous magnetisation also may be derived, do not give much information in our case, mainly on account of the temperature gaps above and below the liquid hydrogen region [note added in the translation].

[3]) Here by „CURIE-temperature" the temperature θ in the relation $\chi(T-\theta) = C$ is meant.

Mathematics. — *"Representation of the Pairs of Points that are Associated relative to a Conic, on the Points of Space"*. (Second communication). By G. SCHAAKE. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of May 30, 1925).

In these Proceedings, XXVIII, p. 267, the author has treated a representation of the pairs of points associated relative to a conic, on the points of space. In the following paper we shall indicate a way of producing the same representation which differs from the one given l.c.

§ 1. The system of the pairs of points of a plane α is a system of ∞^4 individuals, the same as that of the straight lines of space. Both systems have moreover the property in common that we may define their figures by six homogeneous coordinates between which there exists a fundamental relation. For the straight lines of space these are PLÜCKER's coordinates.

In order to find the coordinates of a given pair of points (P_1, P_2) of α we remark that the two pencils of rays that have P_1 and P_2 as vertices, form a degenerate class-conic, i.e. that these two pencils form together a degeneration of the system of straight lines which envelop a conic. The product of the first members of the equations of P_1 and P_2 in line coordinates gives the first member of the equation of the aforesaid class-conic k_2. Hence this equation has the form:

$$p_{11}\,\xi_1^2 + 2p_{12}\,\xi_1\xi_2 + 2p_{13}\,\xi_1\xi_3 + p_{22}\,\xi_2^2 + 2p_{23}\,\xi_2\xi_3 + p_{33}\,\xi_3^2 = 0 \quad . \quad (1)$$

Now we consider the six coefficients p_{ik} as homogeneous coordinates of the pair of points (P_1, P_2). As k_2 is degenerate they must satisfy the relation:

$$\begin{vmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is obvious that inversely six quantities p_{ik} which satisfy the relation (2), define a pair of points of α, the pair of the two points into which the class-conic represented by equation (1), degenerates.

If the homogeneous coordinates of P_1 and P_2 are resp. x_1, x_2, x_3 and x'_1, x'_2, and x'_3, we have:

$$p_{ik} = \tfrac{1}{2}\,(x_i\,x'_k + x_k\,x'_i),$$

hence:

$$p_{ii} = x_i\,x'_i.$$

§ 2. If we consider $p_{11}, \dots, p_{33}$ as homogeneous coordinates of a point Q in R_5, (2) is the equation of a cubic variety of R_5. If we associate to each other the pair of points (P_1, P_2) of α and the point Q of V_4 which have the same homogeneous coordinates, we find a one-one correspondence between the pairs of points of α and the points of V_4 and accordingly a representation of the system of the pairs of points of α on the above mentioned cubic variety [1]).

This representation has neither singular points nor singular conics. By transformation to another system of coordinates in α the formulas of transformation for the p's are also linear. We see, therefore, that the geometry of the pair of points in the plane is identical with that on a cubic variety in R_5.

§ 3. If we have two conics:

$$S_1 \equiv \Sigma\, a_{ik}\, x_i\, x_k = 0 \quad \text{and} \quad S_2 \equiv \Sigma\, b_{ik}\, x_i\, x_k = 0,$$

and if A_{ik} is the minor of a_{ik} in the discriminant of the form S_1,

$$\Sigma\, A_{ik}\, b_{ik} = 0$$

is the condition that must be satisfied if the conic $S_1 = 0$ is to be harmonically inscribed in $S_2 = 0$.

The A's are the coefficients of the class-equation of the conic $S_1 = 0$. Hence

$$\Sigma\, p_{ik}\, a_{ik} = 0$$

is the condition that must be satisfied if the conic $p_\xi^2 = 0$ is to be harmonically inscribed in $a_x^2 = 0$.

Accordingly a linear four-dimensional space R_4 in R_5 represents all the conics p_ξ^2 that are harmonically inscribed in a given conic k^2. The intersection with V_4 is the representation of the system of the pairs of points that are associated relative to k^2. For if we choose a polar triangle of k^2 the conics inscribed in this triangle which have degenerated into a pair of points, always consist of an angular point of this triangle and a point of the opposite side. Accordingly the conics harmonically inscribed in k^2 which have degenerated into a pair of points, always consist of two points associated to each other relative to this conic, and obviously the inverse also holds good.

Consequently the system Σ of the pairs of points associated relative to a conic k^2, is represented on the cubic variety V_3 in which V_4 is cut by R_4. On this variety lies the curve of the image points of the coincidences of Σ, for which P_1 and P_2 coincide in a point of k^2.

The order of this curve is equal to the number of points of intersection with another linear four-dimensional space R'_4, of which the points on V_4 are the images of the pairs of points which are associated to each other relative to another conic k'^2. The points that are common to R_4, R'_4 and V_4 are the images of the pairs of points which are associated to each other relative to k^2 as well as relative to k'^2 and which define, therefore, a quadratic involution in α. This involution contains four coincidences, to wit the points of intersection of k^2 and k'^2; hence the locus on V_3 of the images of the double points of Σ is a biquadratic rational curve k^4. This appears also analytically if we substitute for x_1, x_2 and x_3 in the equations

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[1]) Cf. CAYLEY: On the curves which satisfy given conditions, *Philosophical Transactions of the Royal Society of London*, vol. 158, p. 75, where the representation is treated of the pairs of lines of a plane on a cubic variety in R_5.

$$p_{ik} = x_i \; x_k$$

expressions that are quadratic in a parameter t.

A straight line of V_3 represents a tangential pencil of conics of which all the individuals have degenerated into two plane pencils. The vertices of these pencils form in the first place the associated pairs of points of a line l, which define an involution λ. The image line k of λ is a chord of k^4 as each system λ contains two coincidences. If these coincidences lie in the points A_1 and A_2 of k^2, k is the line which joins the image points K_1 and K_2 on k^4 of these coincidences. As each pair of points associated relative to k^2 belongs to one system λ, we find:

The variety V_3 consists of the chords of k^4.

Further we have systems π of which the pairs consist of a fixed point P and the points of the polar line p of P relative to k^2. These are represented on straight lines s of V_3, which, as a system π does not contain any coincidence, do not have any point in common with k^4. The transition between the systems π and λ is formed by the systems τ which consist of a point T of k^2 and the points of the tangent t to k^2 at T. To a system τ there corresponds a tangent to k^4.

A straight line through a point of k^4 is the image of a special tangential pencil of conics. For an arbitrary straight line the image points of the three degenerations of the corresponding tangential pencil lie in the points of intersection of this line with V_3. In the special case which we considered, one of the conics of the tangential pencil has degenerated into a double point. As we know that this double point counts for two degenerations of the tangential pencil, two of the points of intersection of a line cutting k^4 with V_3 coincide in the intersection of the line with k^4, and k^4 is therefore a double curve of V_3.

§ 4. We choose a point K on k^4 and we project V_3 out of K on a three-dimensional space R^1_3 of R_4. The projection S of a point Q of V_3 on R^1_3 may be considered as the image point of the pair of points (P_1, P_2) of α corresponding to Q. In this way we have found a representation of the pairs of points associated relative to k^2 on the points of R^1_3. The projection k^3 of k^4 out of K on R^1_3 consists of points that are singular for the representation. For if we choose S on k^3, the whole line KS lies on V_3. Consequently S is the image of all the pairs of points of the line BP that are associated relative to k^2 if the coincidences lying in the points B and P of k^2 are resp. represented on K and the other intersection of KS and k^4.

The curve k^3 is the locus of the singular image points. k^3 always contains the image point of one of the ∞^2 pairs of points of which the carriers pass through B.

As k^3 is the projection of k^4 out of K on R_3^1, k^3 is in particular the locus of the image points of the coincidences among the pairs of points associated relative to k^2.

An arbitrary R_3 of R_4 cuts V_3 in a cubic surface Ω which has four conical points in the points of intersection of this R_3 with k^4. The projection of this surface, a cubic surface Ω' with four conical points lying on k^3, is the image of the system of the pairs of points that are associated relative to the conics of a pencil and which form, accordingly, a quadratic involution. If we have a space which touches k^4 at K, two of the conical points of Ω coincide in a biplanar point of this surface. The tangent planes are the planes through the tangent k at K to k^4 and the other two conical points. For an arbitrary plane through k cuts Ω along k and a conic which touches k at K. For each of the two above mentioned planes this conic degenerates into two lines through K one of which passes through another conical point of Ω. Hence any line through K in such a plane has three points of intersection coinciding in K with the intersection of Ω and the plane, so that the pencil in this plane which has K as vertex, consists of tangents of Ω.

The quadratic hypercone of the tangents of V_3 at K is accordingly cut by an R_3 touching k^4 at K along the two planes through k and the two points of intersection outside k of the R_3 with k^4. If k cuts the space R_3^1 in the point A on k^3, these planes are projected out of k on R_3^1 in two generatrices of the cone $\varkappa$ which projects k^3 out of A.

To the coincidence in B there corresponds on V_3 the point K. For the projecting ray we may now choose any tangent to V_3 at K.

Consequently the representation of the pairs of points (P_1, P_2) associated relative to k^2 on the points S of R_3^1, contains one cardinal pair of points, the one for which P_1 and P_2 coincide in B. To this pair the points of the quadratic cone K are associated.

If a point Q of V_3 approaches to the point K of k^4, the chord of k^4 through Q approaches to the chord KL of this curve which lies in the plane through k and the tangent q at K to the curve along which Q approaches to k^4. The pair of points (P_1, P_2) corresponding to Q approaches to the coincidence in B, so that the line $P_1 P_2$ approaches to the join of B and the point P of k^2 which corresponds to the point L of k^4. The tangent q which is the limiting position of the projecting line KQ, cuts R_3^1 in a point of the generatrix of $\varkappa$ which joins A to the point of k^3 that corresponds to P.

To a pair of points for which P_1 and P_2 coincide in B and $P_1 P_2$ is defined, there correspond accordingly the points of a generatrix of $\varkappa$. This generatrix joins A and the point of k^3 which corresponds to the point different from B where $P_1 P_2$ cuts k^2.

§ 5. The intersection of a space touching k^4 at K with V_3, the surface Ω, has the line KK_1 which joins the biplanar point K to a conical point K_1, as torsal line. By making two conical points of an arbitrary surface Ω approach K we can easily see that the plane through KK_1 and k becomes a tangent plane to Ω at all points of KK_1.

In the same way the intersection of V_4 with the space through KK_1 which touches k^4 at K_1, has the line KK_1 as torsal line, and the plane through KK_1 and the tangent k_1 to k^4 at K_1 becomes a tangent plane to the surface. Hence V_3 has the same tangent space along a chord of k^4, the space which is defined by the tangents to k^4 at the points where this chord cuts k^4.

The tangent spaces of V_3 along the generatrices of this variety through K cut R_3^1 along the tangent planes of $\varkappa$ through A.

To a system of ∞^1 pairs of points associated relative to k^2 containing a pair for which P_1 and P_2 do not coincide and the carrier passes through B, there corresponds a curve on V_3 which cuts a generatrix of V_3 through K. The projection of this curve must touch $\varkappa$ at the projection on k^3 of the point of intersection.

If the image curve in R_3^1 of such a system cuts k^3 but does not touch $\varkappa$ at this point of intersection, this point is the image of a coincidence. For the point of the curve which corresponds to this curve on V_3 of which the aforesaid point of intersection is the projection, must necessarily lie on the double curve of this variety.

Analogous remarks may be made about the image surface of a system of ∞^2 pairs of points that are associated relative to k^2.

§ 6. A system λ of the ∞^1 pairs of points of a line l associated relative to k^2, is represented on a chord of k^4 which is projected out of K in a chord of k^3.

Accordingly the system λ of the ∞^1 pairs of points of a line l which are associated relative to k^2, is represented on a chord of k^3.

A system π which consists of the pairs of points associated relative to k^2 for which one point lies in a given point P and the other, therefore, on the polar line p of P, is represented on a straight line of V_3 that does not cut k^4. This line cuts a generatrix of V_3 through K in the image point of the pair that consists of P and the intersection of BP and p. Consequently its projection s on R_3 touches $\varkappa$ on k^3 at the point which corresponds to the point of intersection outside B of the line BP and k^2.

A system π is represented on a line s which touches $\varkappa$ on k^3.

§ 7. The representation of the pairs (P_1, P_2) on the points S of R_3^1 may also be brought about without more-dimensional considerations. We consider the one-one correspondence between the points of k^2 and those of k^3. The image point S of (P_1, P_2) must lie on the chord k of k^3 corresponding to the system λ of $P_1 P_2$ and on the two lines s which correspond to the systems π that are defined by P_1 and P_2. The chord k joins the points of k^3 which correspond to the points of intersection of $P_1 P_2$ and k^2. The lines s lie in the tangent planes of $\varkappa$ at those points of k^3 that are associated to the points of intersection outside B of BP_1 and BP_2 with k^2.

The image point S is a common point of the two above mentioned tangent planes and the chord k.

If k^2 is the projection of k^3 on a plane α out of a point A of k^3 and if the corresponding points of k^3 and k^2 always lie on a projecting ray, hence on a generatrix of $\varkappa$, the projections of the lines s on α are the tangents to k^2 at the points of intersection outside B of BP_1 and BP_2 with k^2. The intersection of these tangents lies on P_1P_2. For the pairs (K_1, K_2) of these points of intersection which may be derived from the pairs (P_1, P_2) of the involution defined on $P_1P_2 = l$ by k^2, form an involution on k^2 of which the double points lie in the points of intersection of l with k^2 and which, accordingly, has l as axis.

The point S, i.e. the intersection of the lines s, has the intersection of the two aforesaid tangents as projection and lies moreover on the chord k of k^3 corresponding to $P_1 P_2$, i.e. the chord k of k^3 that does not pass through A, lying in the plane through A and $P_1 P_2$.

In this way we have come back to the way of producing our representation which has been treated in the paper mentioned at the beginning.

Mathematics. — *"An Involution in the Rays of Space through which a Quadratic Scroll is Associated to a Plane Pencil"*. By G. SCHAAKE.

(Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of May 30, 1925).

§ 1. We start from a linear complex C, a straight line m which does not belong to C, and a straight line n lying in C. By the aid of these we can associate to any line l of space a line l' in the following way.

We consider the scroll ϱ defined by l, m and n. This has one more straight line o in common with C besides n. We associate to l the generatrix l' of ϱ which is harmonically separated from l by m and o. The ∞^4 pairs of rays (l, l') define an involution I in the rays of space.

§ 2. If l is chosen in n, there are ∞^3 scrolls ϱ, hence ∞^3 lines l'. Accordingly a complex N of lines n' is associated to n in our involution of rays I.

In order to find the number of generatrices n' of N in a given plane pencil (T, τ), we remark that a straight line n' lying in (T, τ) belongs to a scroll ϱ which has the transversal t_1 of m and n through T and the transversal t_2 of m and n lying in τ as directrices, as t_1 and t_2 must cut at least three straight lines in ϱ.

Consequently the straight line o corresponding to n', which is at the same time a generatrix of ϱ, must lie in the plane pencil which has as vertex the point T' which is harmonically separated from the point $t_1 m$ by T and the point $t_1 n$ and of which the plane passes through t_2. As this line o must belong to C, the pencil in question contains only one line o, which corresponds to a straight line n' of (T, τ). Accordingly (T, τ) contains only one line n' of N so that N is a linear complex.

In order to find the plane pencil of N that has an arbitrary point T of space as vertex, we consider the transversal t_1 of m and n through T and we determine the point on t_1 that is harmonically separated from the point of intersection of t_1 and m by T and the intersection of t_1 and n. The plane of the pencil of C that has this point as vertex, contains the transversal t_2 of m and n. The plane through T and t_2 is, therefore, the plane of the pencil of N that has T as vertex.

If we have a straight line n' which cuts n, the scroll through m and n containing n' must degenerate into a plane pencil ψ containing n and a plane pencil φ containing m which has one ray in common with ψ.

If ψ does not belong to C, o lies in φ but not in ψ and the same holds good for the line n', that is harmonically separated from o and m by the line $\varphi\psi$, so that in this case we do not get a straight line cutting n.

If, however, ψ belongs to C, all the complex rays in ψ may be considered as lines o and also as lines n', as each line n' is harmonically separated from n by o and the line that is common to φ and ψ. Accordingly N has all the plane pencils containing n in common with C.

The line n is, therefore, for I a singular line of the third rank[1]). *To n there corresponds a linear complex N which contains the special bilinear congruence Γ of the lines of C that cut n.*

To any line l of a plane pencil ψ containing n, there corresponds as line l' the generatrix of the plane pencil φ corresponding to ψ which is harmonically separated from the lines m and o in φ by the line $\varphi\psi$. As there are ∞^2 plane pencils ψ containing n, we find ∞^2 singular lines, which all cut m and, as they also correspond to n in I, belong to N.

Accordingly the bilinear congruence B of the lines of N that cut m, consists of straight lines that are singular for I. To each of these lines a plane pencil containing n is associated. To each line cutting n there corresponds a line of B.

For a straight line l which belongs to a plane pencil ψ of C containing n, all the lines of ψ are lines o, hence also lines l'.

Consequently the lines of the special bilinear congruence Γ of the rays of C which cut n, are also singular for our representation. To each line of Γ there correspond as lines l' all the lines of the plane pencil of this congruence which contains l.

If we choose l in m there are ∞^3 scrolls ϱ, but on each of these scrolls the line l' which is harmonically separated from l by m and o, coincides with l.

Hence the line m is an isolated double ray of our involution and C consists wholly of double rays.

§ 3. For the rays l belonging to a given plane pencil (T, τ) the scroll ϱ always has as directrices the transversal t_1 through T of m and n and the transversal t_2 of these lines lying in τ. Hence the scroll λ associated to (T, τ) belongs to the bilinear congruence that has t_1 and t_2 as directrices. As (T, τ) has one ray in common with the linear complex N and contains one line which cuts n, n is a generatrix of λ and this surface has one line in common with the bilinear congruence B. The lines o corresponding to the lines l of (T, τ) form the scroll π of C that has t_1 and t_2 as directrices.

Through a point of t_1 there passes only one generatrix of λ, the generatrix of the scroll ϱ which is defined by l, m and the line of π passing through the point of t_1 that is harmonically separated from the intersection of t_1 and m by T and the chosen point.

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[1]) A singular straight line of the rank n is a straight line to which ∞^n rays are associated.

37

Suppose that through a point of t_2 there pass x lines of λ; in this case this scroll is of the order $x+1$, the same as the surface that is associated to the plane pencil which has a point on t_2 as vertex, which surface has t_2 as single and t_1 as x-fold directrix. The two scrolls have $(x+1)^2 - 2x = x^2+1$ generatrices in common. These are in the first place the line n and further the line l' which is associated to the common line l of the two plane pencils. Hence $x^2+1 \doteq 2$ or $x=1$.

Consequently to a plane pencil of lines l *there corresponds a quadratic scroll of lines* l' *which contains* n *and has one line in common with the bilinear congruence* B [1]).

If (T, τ) contains one line of B, a plane pencil containing n splits off from the associated scroll and there remains a plane pencil that has one line in common with B.

For a line l cutting m ϱ degenerates into a plane pencil φ containing m and a plane pencil ψ containing n. The line o lies in φ the same as l', which line is harmonically separated from l by m and o. A plane pencil with vertex on m, which accordingly contains one line of B, is therefore transformed into a plane pencil that has the same vertex. In the same way it appears that to a pencil in a plane through m, there corresponds a pencil in the same plane and that a plane pencil containing m is transformed into itself.

If (T, τ) has a straight line in common with Γ, the plane pencil of Γ which contains this line, splits off from λ. n belongs to this pencil and it has a line in common with B as it lies in the linear complex N together with B. Accordingly there remains a plane pencil that has no line in common with B but that has a line in common with Γ. This line lies in the plane pencil of Γ which contains the common line of (T, τ) and Γ.

We saw that to a line l cutting n there corresponds a line which passes through the point of intersection of the plane (n, l) with m and which lies in the plane through m and the point ln. If, therefore, we have a plane pencil with vertex on n, a pencil of B corresponds to it which lies in the plane through m and the vertex on n and of which, accordingly, the vertex lies on the line m' which is associated to m relative to the complex N. On the contrary to a pencil of lines l of which the plane passes through n, there corresponds a pencil of B of which the vertex lies in the intersection of m and the plane through n, and which lies in a plane through m'.

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[1]) Another involution of rays, which transforms a plane pencil into a quadratic scroll, has been indicated and investigated by Prof. JAN DE VRIES, these Proc., XXII, p. 462. In this involution, however, the image of a sheaf is not a bilinear congruence, but a congruence (3,1).

§ 4. To a sheaf of lines l with vertex P there corresponds a congruence Σ of lines l' that has the transversal p of m and n through P as directrix, as this line is a directrix of all the scrolls ϱ of the lines l of the sheaf P. For a line l through P of which the associated line l' passes through a given point Q, the scroll ϱ must also have the transversal q of m and n through Q as directrix. Hence such a line l must lie in the pencil that has P as vertex and of which the plane passes through q. One generatrix of the scroll λ corresponding to this pencil passes through Q. The sheaf-order of Σ is accordingly one.

In the same way the pencil that has P as vertex and which lies in a plane through the transversal b of m and n in a plane β, must contain each line l through P for which the associated line lies in β. One generatrix of the scroll λ corresponding to this pencil lies in β. Accordingly the field-order of Σ is also one.

The congruence Σ contains n, as this line is associated to the plane pencil of lines l which the sheaf P has in common with the complex N. As further the sheaf P contains a pencil of lines l in a plane through n, Σ has in common with B a pencil with vertex in the intersection M of p and m in a plane through m'. Σ also contains the plane pencil of Γ which contains the line of Γ through P.

To a sheaf P there corresponds accordingly a bilinear congruence Σ which contains n, has a pencil in common with B that has its vertex on m and lies in a plane through m', and has a pencil in common with Γ.

The lines of Σ through P form the plane pencil of double rays belonging to C which has this point as vertex. The directrix of Σ different from p is the transversal of n and m' lying in the plane of this pencil.

If P lies on n there corresponds to the sheaf a pencil of singular lines belonging to B in a plane through m and P of which the vertex lies on m'.

As to a line cutting m there corresponds a ray which cuts m in the same point, a sheaf with vertex on m is transformed into itself.

If P lies on m' there splits off from the corresponding bilinear congruence the sheaf of which the vertex S lies in the intersection of n with the plane through m and P, as this sheaf corresponds to the plane pencil which the sheaf P has in common with the congruence B. Consequently there remains a field of rays that must have a pencil in common with B in a plane through m', so that the plane of this field is the plane (S, m').

From the field-order of the congruences Σ, i.e. the number of pairs of the involution of which one line passes through a given point and the other lies in a given plane, it ensues that to a field of rays α there corresponds a congruence Φ with sheaf-order one. For the pairs of rays (l, l') of which l lies in α and l' in a plane β, the scrolls ϱ have the transversals a and b of m and n in these planes as directrices, so that l lies in the plane pencil in α which has the intersection of b with α as vertex. The plane β through b contains one generatrix of the scroll corresponding to this pencil. Accordingly the field-order of Φ is also one.

Φ contains again n and the plane pencil of Γ to which the ray of Γ in α belongs. But α contains a plane pencil with vertex on n, so that Φ has a pencil in common with B in a plane through m of which the vertex lies on m'. The plane of the latter pencil passes at the same time through the point of intersection of α and n.

Consequently to a field of rays α *there corresponds a bilinear congruence* Φ *containing* n *which has a pencil in common with* B *with vertex on* m' *and lying in a plane through* m, *and which has a plane pencil in common with* Γ.

The rays of Φ in a are double rays of our involution and form the pencil of C in this plane. The transversal of m and n through the vertex of this pencil is the directrix of Φ different from a.

If α passes through n there corresponds to the field a plane pencil of singular lines belonging to B. The vertex of the pencil lies in the point of intersection of m and α, its plane passes through m'.

A field containing m is transformed into itself because to a line l cutting m there corresponds a ray in the plane (m, l).

If α passes through m' there splits off from the associated bilinear congruence the field of rays of which the plane σ is defined by n and the point of intersection of α and m, as this field corresponds to the pencil of B lying in α. Accordingly there remains a sheaf of rays which must have a plane pencil in common with B of which the vertex lies on m', so that the vertex of the sheaf associated to α lies in the point of intersection of this line with σ.

§ 5. As a linear complex L has two straight lines in common with a scroll λ, the corresponding complex Λ contains two generatrices of any plane pencil. Hence Λ is quadratic. The complex Λ contains n, as this line is associated to all the lines which L has in common with N. Accordingly a plane pencil containing n to which there corresponds a line of B, generally outside L, does not contain any line of Λ besides n, so that n is a double line of this complex.

As L has one line in common with any plane pencil containing n and with any plane pencil of Γ, the congruences B and Γ belong wholly to Λ.

The lines of Λ issuing from a point P of n, form the plane pencil of Γ which has P as vertex, and the plane pencil corresponding to the line which L has in common with the pencil of B in the plane (P, m).

To a linear complex L *there corresponds a quadratic complex* Λ *which contains the congruences* B *and* Γ *and which has* n *as double line.*

If L contains the line n, the linear complex Λ containing n, B and Γ

splits off from N and, accordingly, there remains a linear complex to which n belongs.

A linear complex containing B or Γ always becomes such a complex.

If L is a special complex with axis a, Λ consists of congruences Σ as well as of congruences Φ. The directrices of the congruences Σ form two scrolls of which the first has a, m and n as directrices, the second a', m' and n, if a' is the straight line associated to a relative to C. In this way the directrices of the congruences Φ form two scrolls of which the first has a, m and n, the second a', m and n as directrices.

§ 6. We consider a scroll $\varkappa$ of the order μ which has n as ν-fold line and which contains resp. β and γ lines of B and Γ. This has in common with the quadratic complex Λ corresponding to a linear complex, $2\mu-2\nu-\beta-\gamma$ lines that are not singular for the involution, which number indicates the order of the scroll $\varkappa'$ corresponding to $\varkappa$. As $\varkappa$ has $\mu-\nu-\beta-\gamma$ lines outside B and Γ in common with N, $\varkappa'$ contains the line n as $\mu-\nu-\beta-\gamma$-fold generatrix. The number of generatrices of $\varkappa$ that are not singular for our involution, i. e. the number of these lines which belong at the same time to the special linear complex with axis n, is $\mu-2\nu-\gamma$. Further there corresponds to any common line of $\varkappa$ and Γ a line of $\varkappa'$ which belongs at the same time to Γ.

To a scroll of the order μ which has n as ν-fold line and which contains resp. β and γ lines of B and Γ, there corresponds a scroll of the order $2\mu-2\nu-\beta-\gamma$ which has a $\mu-\nu-\beta-\gamma$-fold generatrix in n and which has $\mu-2\nu-\gamma$ lines in common with B and γ lines different from n in common with Γ.

Accordingly to an arbitrary scroll of the order μ there corresponds a scroll of the order 2μ which has a μ-fold generatrix in n and which has μ lines in common with B.

Let us now examine the congruence Ψ' corresponding to a congruence Ψ (s, v) which has a p-fold line in n, which has a scroll in common with B of which m is an a-fold, m' a b-fold directrix and which contains c generatrices of any plane pencil of Γ.

Ψ has resp. $s+v-p-a-c$ and $s+v-p-b-c$ non-singular generatrices in common with a congruence Σ and a congruence Φ. Hence a plane pencil of B with vertex on m, to which there corresponds a field of rays containing n, contains $v-p-c$, a pencil of B in a plane through m, to which a sheaf with vertex on n is associated, contains $s-p-c$ lines of Ψ'.

Through a point of n there pass b non-singular lines of Ψ', in a plane through n there lie a non-singular lines of the congruence, as a sheaf with vertex on n and a field through n correspond resp. to a plane pencil of B with vertex on m' and a plane pencil of B with vertex on m.

Consequently to a congruence Ψ with sheaf-order s and field-order v with a p-fold line in n which has a scroll in common with B for which

m is an a-fold, m' a b-fold directrix, and which contains c generatrices of any plane pencil of Γ, there corresponds a congruence Ψ' with sheaf-order $s+v-p-a-c$ and field-order $s+v-p-b-c$ which has a scroll in common with B that has m as $v-p-c$-fold, m' as $s-p-c$-fold directrix, which contains c lines of any plane pencil of Γ and has an $s+v-p-a-b-2c$-fold line in n.

Ψ' has as many plane pencils in common with Γ as Ψ contains lines of Γ that are not singular for the involution, hence $s+v-2p$.

Accordingly to an arbitrary congruence $\Psi(s, v)$ there corresponds a congruence $\Psi(s+v,\ s+v)$, which has a scroll in common with B that has m as v-fold, m' as s-fold directrix, and which has an $s+v$-fold generatrix in n. Ψ' has $s+v$ plane pencils in common with Γ.

Finally we examine the complex K' which corresponds to a complex K of the order $\varkappa$ of which the rays of the congruences B and Γ are resp. δ- and ε-fold lines, and which has n as π-fold line.

The complex K contains $2\varkappa-\pi-\delta$ generatrices of a scroll λ. A plane pencil containing n has δ lines of K' besides n, so that n is a $2\varkappa-\pi-2\delta$-fold line of K'. A plane pencil which contains a line of B and to which such a plane pencil is associated, has $\varkappa-\delta$ lines in common with K which are not singular for I. Hence the lines of B are $\varkappa-\pi$-fold lines of K'. In the same way it ensues from the fact that a plane pencil through a line of Γ contains $\varkappa-\varepsilon$ lines of K, non-singular for I, that the lines of Γ are $\varkappa-\pi-\delta+\varepsilon$-fold lines of K'.

Accordingly to a complex K of the order $\varkappa$ that has n as π-fold line and of which the rays of the congruences B and Γ are resp. δ- and ε-fold lines, there corresponds a complex K' of the order $2\varkappa-\pi-\delta$ which has n as $2\varkappa-\pi-2\delta$-fold line and of which the rays of B and Γ are resp. $\varkappa-\pi$- and $\varkappa-\pi-\delta+\varepsilon$-fold lines.

Hence an arbitrary complex K of the order $\varkappa$ is transformed into a complex K' of the order $2\varkappa$ which has n as $2\varkappa$-fold line and of which the rays of B and Γ are $\varkappa$-fold lines. The lines of K' passing through a point of n form, therefore, besides a plane pencil of Γ, a cone of the order $\varkappa$.

§ 7. The involution of rays examined in this paper may e.g. be applied to determine the numbers of scrolls λ that contain a given line n, have a line in common with a congruence B and which satisfy besides a five-fold condition.

Let us try to find e.g. the number of the scrolls λ which contain a line l and which pass through two given points. By means of our involution these scrolls are transformed into the plane pencils through a given line l' which have a straight line in common with each of two bilinear congruences Σ_1 and Σ_2. We find the number of these plane pencils by considering the correspondence on l' which arises in the following way. Through a point P of l' we draw the line s_1 of Σ_1. To P we associate the point P' where l' is cut by the generatrix of Σ_2 in the plane (l', s_1).

The (1,1) correspondence (P, P') has two coincidences.

Accordingly there are two scrolls which contain two given straight lines, have one ray in common with a bilinear congruence, and pass through two given points.

We can also try to find the number of the scrolls λ which contain a line l and have a straight line in common with a plane pencil w_1. The corresponding plane pencils must pass through l' and have a straight line in common with the scroll λ_1 corresponding to w_1. Their vertices lie in the points of intersection of l' and λ_1.

Consequently there are two scrolls with two given generatrices which have one line in common with a bilinear congruence and with a plane pencil.

Chemistry. — *"Equilibria in systems in which phases, separated by a semi-permeable membrane"* X. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of June 27, 1925).

Systems with several semipermeable membranes. Double-membranes.

We now take the osmotic equilibrium:

$$E = E_1 \mid E_2 \mid E_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the separate systems E_1 and E_2 and also E_2 and E_3 are separated from one another by a semipermeable membrane. Of the many possible cases we now shall consider only the case, that the two semipermeable membranes allow to pass one substance only viz. the same substance W (water). We find the equations for equilibrium by expressing:

a. that the phases of the system E_1 are in equilibrium, taken for themselves; also those of E_2 and those of E_3.

b. that the O. W. A. of E_1 is equal to that of E_2 and that of E_2 equal to that of E_3; consequently the three separate systems have the same O. W. A.

Consequently we get the same equations for equilibrium, independent which of the three separate systems in (1) is situated between the two membranes. Therefore, if one of the three osmotic systems:

$$E_1 \mid E_2 \mid E_3 \qquad E_2 \mid E_1 \mid E_3 \qquad E_1 \mid E_3 \mid E_2$$

forms an osmotic equilibrium, then both the other ones do also.

In fig. 1 in which only a part of triangle WXY is drawn, the lines drawn represent isotonic curves. We now take into consideration the osmotic system.

$$L_1 \mid L_2 \mid L_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which L_1 L_2 and L_3 are liquids, represented by the points 1, 2 and 3. It is apparent from the situation of those points that

$$\text{O.W.A. or } L_1 < \text{O.W.A. or } L_2 < \text{O.W.A. or } L_3.$$

Consequently we may write for (2):

$$L_1 \overset{|}{\underset{|}{\rightarrow}} L_2 \overset{|}{\underset{|}{\rightarrow}} L_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the arrows indicate the direction in which the substance W

water) diffuses. Consequently in fig. 1 the liquids L_1 and L_3 move in the direction of the arrows, drawn in the points 1 and 3; we shall refer later to the movement of L_2, which takes place of course along the line $2W$.

At last a definite osmotic equilibrium shall be formed from system (3); then the three liquids are situated on an isotonic curve. It may be converted f.i. into one of the osmotic equilibria:

$$L_c \mid L_b \mid L_a \text{ or } L_h \mid L_g \mid L_f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and accidentally also into:

$$L_e \mid L_2 \mid L_d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that liquid L_2 at the finish of the osmose is again the same as at the beginning.

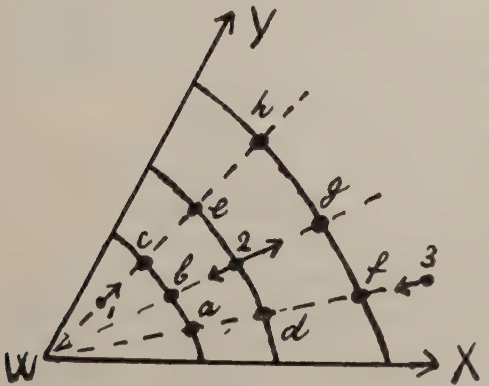

Fig. 1.

If, besides the compositions, still also the quantities n_1, n_2 and n_3 of the liquids $L_1 L_2$ and L_3 are known, then we know also the quantities n'_1 n'_2 and n'_3 and the compositions of the liquids L'_1 L'_2 and L'_3 which arise at last. We represent the composition of L_1 by

$$x_1 X + y_1 Y + (1 - x_1 - y_1) W$$

that of L'_1 by

$$x'_1 X + y'_1 Y + (1 - x'_1 - y'_1) W$$

those of the other liquids by substituting the index 1 by 2 and 3. As the quantity of water in the whole system must remain constant and also the quantities of X and Y in each of the three separate systems, we find the equations:

$$\left.\begin{array}{ccc} & n_1 + n_2 + n_3 = n'_1 + n'_2 + n'_3 & \\ n_1 x_1 = n'_1 x'_1 & n_2 x_2 = n'_2 x'_2 & n_3 x_3 = n'_3 x'_3 \\ n_1 y_1 = n'_1 y'_1 & n_2 y_2 = n'_2 y'_2 & n_3 y_3 = n'_3 y'_3 \end{array}\right\} \quad . \quad (6)$$

Further we still have the two equations:

$$\varphi'_1 = \varphi'_2 = \varphi'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which

$$\varphi = \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y};$$

they express that the three liquids L'_1 L'_2 and L'_3 are in osmotic equilibrium at last. We now have 9 equations for the definitions of the 9 unknowns which occur in (6) and (7); the quantities and compositions of L'_1 L'_2 and L'_3 are defined, therefore. From this appears also that the result of the osmose depends not only on the composition of the original liquids, but also on the ratio of their quantities.

The quantity of a substance W, which diffuses in a definite time by a membrane, depends not only on the difference of the O.W.A. of the two liquids, but also on the active surface of the membrane. By changing this surface, we may, therefore, regulate also the quantity of water, which diffuses in a definite time through this membrane.

Let us assume now that the system:

$$L_1 \overset{|}{\underset{|}{\rightarrow}} L_2 \overset{|}{\underset{|}{\rightarrow}} L_3 \text{ is converted into } E = L_c \mid L_b \mid L_a \quad \text{(fig. 1).}$$

As L_1 only gives water and L_3 only takes water in, those two liquids shift during the osmose always in the same direction viz. L_1 from point 1 towards c and L_2 from point 3 towards a (fig. 1). Although liquid L_2 arrives at last from point 2 in b, we yet may distinguish different cases.

a. L_2 goes without change in direction from 2 towards b.

b. L_2 goes starting from point 2 firstly in the direction towards g, returns then towards point 2 and goes further towards b.

c. L_2 goes starting from point 2 firstly towards point b, then a little further in the direction towards W and returns then towards b.

In both the latter cases we shall say that the liquid varies or swings; in case b it swings over point 2, in case c over point b.

The case, mentioned sub b, may be realised when we regulate the surface of the two membranes in such a way, that at the beginning more water diffuses from L_2 towards L_3 than L_2 takes from L_1. The case mentioned sub c can occur when the membrane between L_1 and L_2 is very large and the quantity of L_1 is large with respect to the quantity of L_2. Corresponding phenomena can occur, when system (3) is converted into one of the other equilibria (4) and (5).

If we let the liquids change places in system (2) then we get:

$$L_2 \overset{|}{\underset{|}{\leftarrow}} L_1 \overset{|}{\underset{|}{\rightarrow}} L_3 \qquad (8a) \qquad\qquad L_1 \overset{|}{\underset{|}{\rightarrow}} L_3 \overset{|}{\underset{|}{\leftarrow}} L_2 \quad . \; . \; . \quad (8b)$$

in which the arrows indicate again the direction in which the water diffuses at the beginning of the osmose. With a single example we shall show that the liquids in those systems may swing during the osmose. Let us assume that in (8a) the osmose between L_1 and L_3 takes place extremely slowly, but that between L_2 and L_1 extremely quickly. As the osmotic equilibrium between L_2 and L_1 is reached then practically almost immediately, we then get a system:

$$L'_2 \mid L'_1 \mid L'_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8c)$$

in which L'_3 differs only very little from L_3, L'_2 and L'_1 now have almost the same O.W.A., which is larger than that of L_1 but smaller than that of L_2, also smaller than that of L_3 or L'_3, therefore. Water now shall diffuse, as is indicated in:

$$L'_2 \overset{|}{\underset{|}{\rightarrow}} L'_1 \overset{|}{\underset{|}{\rightarrow}} L'_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \tag{8d}$$

viz. firstly from L'_1 towards L'_3 and afterwards from L'_2 towards L'_1. The liquid L_2 in (8*a*), therefore, takes water in at the beginning of the osmose, but later it gives water again.

The equations (6) and (7) are valid not only for the conversion of system (3) but also for the systems (8*a*) and (8*b*). Consequently for the end-equilibrium it is indifferent which of the three liquids is between the two membranes; this has influence only on the way in which this equilibrium is formed.

In the osmotic system:

$$L_1 \Big| L_2 \Big| L_3 \Big| L_4 \Big| \; . \; . \; . \; . \; . \; L_n \; . \; . \; . \; . \; . \; . \tag{9}$$

we have n liquids and $n-1$ membranes. We are able to show also that the osmotic equilibrium which arises at last from this, depends only on the quantities and the composition of the liquids, but that it is independent on their series. The way, in which the equilibrium sets in is dependent, however, on the series of the liquids and also on the surface of the membranes.

Let us assume that the O.W.A. of the liquids in (9) increases, according the index of the liquid being larger. We then have:

$$L_1 \overset{|}{\underset{|}{\rightarrow}} L_2 \overset{|}{\underset{|}{\rightarrow}} L_3 \overset{|}{\underset{|}{\rightarrow}} \; . \; . \; . \; . \; . \; . \overset{|}{\underset{|}{\rightarrow}} L_{n-1} \overset{|}{\underset{|}{\rightarrow}} L_n \; . \; . \; . \; . \tag{10}$$

in which the arrows indicate the direction in which the water diffuses. We now may imagine that L_1 and L_n during a long time change their O.W.A. only imperceptibly or not; this can take place f.i. when both liquids are present in a very large excess. This may be the case also when L_1 is f.i. water and L_n watervapour under a very low constant pressure.

While L_1 en L_n then remain unchanged, the other liquids change their composition until the same quantity of water diffuses through each membrane in the same time. As soon as this stationary state has established itself, all liquids have a definite composition and O.W.A. This stationary state depends not only on the original composition and quantities of the different liquids, but also on the surface of the different membranes.

A similar stationary state shall occur also when the liquids $L_2\, L_3 \ldots L_{n-1}$ have the same O.W.A. at the beginning; further, of course it is indifferent whether those liquids have the same composition or not and which substances they contain.

Double-membranes.

If we compare the two osmotic systems:

$$L_1 \mid L_2 \text{ and } L_1 \mid D \mid L_2 \quad . \; . \; . \; . \; . \; . \; . \qquad (11)$$

with one another, then we see that in the first one the two liquids L_1 and L_2 are in osmotic contact with one another with the aid of a single semipermeable membrane; in the second one the water, in order to diffuse from L_1 towards L_2, must pass through two semipermeable membranes, between which a phase (or system) D is found.

We now may consider the two semipermeable membranes with the included phase D as to form together a new semipermeable membrane; we call this "double-membrane with the phase D" or only "double-membrane" and we shall represent it by $\mid D \mid$ or $\mid\,\mid$.

We now may say that the liquids L_1 and L_2 in the second system (11) are in osmotic contact with one another with the aid of a double-membrane. Further we shall see that a double-membrane sometimes may play quite a different part as the single membrane.

We now take the osmotic system:

$$L_1 \mid Y \mid L_2 \quad \text{fig. 1 Comm. III.} \; . \; . \; . \; . \; . \; . \qquad (12)$$

in which L_1 and L_2 are separated from one another by a double-membrane with the solid substance Y. The liquids L_1 and L_2 are represented by points within the field $WwvX$ of fig. 1 Comm. III. Further we shall see that system (12) may pass into one of the osmotic equilibria:

$$E = L'_1 \mid L \mid L'_2 \qquad (13a) \qquad E = L'_1 \mid Y + L_w \mid L'_2 \; . \; . \; (13b)$$

in which all liquids are isotonic, therefore, or into the complex

$$K = L'_1 \mid Y \mid L'_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (14)$$

in which the two liquids are not isotonic. In the latter case, therefore, the double-membrane plays the part of a wall, which is impermeable for water.

As the result of the osmose depends on the composition of the liquids L_1 and L_2 we distinguish three cases.

1. L_1 and L_2 are situated both within the field Wwm fig. 1 Comm. III. The O.W.A. of the solid substance Y is, therefore, greater than that of the liquids L_1 and L_2; at the beginning of the osmose water shall diffuse, therefore, as well from L_1 as from L_2 towards the solid substance Y. Consequently there arises a system:

$$L_1 \mathrel{\mid\!\!\!\rightarrow} Y \mathrel{\leftarrow\!\!\!\mid} L_2 \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (15)$$

It depends on the ratio of the quantities of L_1 L_2 and solid Y what shall occur further. When the quantity of solid Y is very large (in ratio to the quantities of L_1 and L_2) then equilibrium (13*b*) is formed; L'_1 and L'_2 are represented then by points of the isotonic curve *wm*.

When however the quantity of solid Y, is so small that a liquid is formed between the membranes, then an equilibrium (13*a*) arises; the three liquids are situated then anywhere within the region $W w m$ on an isotonic curve; liquid L is situated anywhere between w and W.

2. L_1 and L_2 are both situated within the field $w m X v$. fig. 1 Comm. III.

As the O.W.A. of the solid substance Y is smaller now than that of both the liquids, neither from L_1 nor from L_2 water can diffuse towards Y, therefore. Consequently the double-membrane prohibits the diffusion of water from L_1 towards L_2 and reversally; consequently it behaves itself now as a membrane, which checks water. Consequently the osmotic system (12) remains unchanged.

3. L_1 is situated in the field $W w m$ and L_2 in the field $w m X v$ of fig. 1 Comm. III.

Now water diffuses from L_1 towards the solid substance Y, so that the system $Y + L_w$ arises between both the membranes; water now diffuses from L_w towards L_2. In the beginning of the osmose is formed, therefore, the system:

$$L_1 \overset{|}{\underset{|}{\rightarrow}} Y + L_w \overset{|}{\underset{|}{\rightarrow}} L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It depends on the ratio of the quantities of L_1 L_2 and solid Y what shall occur further. We now may distinguish three cases.

a. An equilibrium (13*a*) is formed; then the three liquids are situated on an isotonic curve with the field $W w m$.

b. The equilibrium (13*b*) is formed; the three liquids are situated on the curve $w m$.

c. The osmotic complex (14) is formed; then L'_1 is situated in curve $w m$ and L_2' anywhere within the field $w m X v$. Consequently no water diffuses more from L'_1 towards L'_2, notwithstanding the O.W.A. of L'_2 is greater than that of L'_1. Consequently in the beginning the double-membrane allows water to diffuse, but it behaves itself afterwards as a membrane, which prohibits the diffusion of the water.

This case can occur when the quantity of L_1 is small with respect to the quantities of L_2 and solid Y.

Till now we have discussed only which osmotic system is formed from (12) at the end of the osmose; in similar way as in the beginning of this communication, the reader can examine for each case, which changes the liquids shall undergo viz. whether they will shift continually towards their state of equilibrium or will swing.

As is apparent from the previous, we may distinguish three cases for the osmotic action of the double-membrane.

1. The water diffuses through the double-membrane, so that an osmotic equilibrium is formed. The double-membrane behaves itself with respect to the water-diffusion as a single membrane. This is the case when both the liquids are situated within the field *W w m* and may take place also when the liquids are situated on different sides of the curve *w m*.

Yet there is a difference between the equilibrium which is formed with the aid of a single membrane and that which is formed with the aid of a double-membrane; sometimes this difference can be very great.

When L_1 and L_2 are situated in the field *W w m*, then the result of the osmose is, that both liquids are situated also within the field *Wwm*; the one viz. shifts away from point *W* and the other towards point *W*, till they arrive on the same osmotic curve.

If, however, we use the double-membrane $\mid Y \mid$ with a large quantity of *Y*, then, as we have seen above, both liquids shift at last towards the isotonic curve *w m*. (fig. 1 Comm. III).

2. The double-membrane prohibits the diffusion of the water; it behaves itself, therefore, as a wall, which checks the water, notwithstanding the two liquids have a different O.W.A.

This is the case, when both liquids are situated in the field *w m X v* (fig. 1 Comm. III).

3. The water diffuses firstly through the double-membrane; then the diffusion stops, although the O.W.A. of both the liquids is still different. This case may occur, when both liquids are situated on different sides of curve *w m*.

We now take the osmotic system

$L_1 \mid Y \mid L_2$ fig. 1 Comm. V. . . . . . . (17)

in which L_1 and L_2 represent liquids of the field *W a c b*. Also here for (17) is valid, what is deduced above for system (12); of course we now have to replace the isotonic curve *w m* and the fields *Ww m* and *wm Xv* of fig. 1 Comm. III by the isotonic curve *a m* and the fields *W a m* and *a m b c* of fig. 1 Comm. V.

If the double-membrane contains the solid substance *X*, then we have the osmotic system:

$L_1 \mid X \mid L_2$ fig. 1 Comm. V . . . . . . (18)

then the isotonic curve *b d* and the fields *W b d a* and *b c d* play a corresponding part.

Hence is apparent that the solid substance, which is present in the double-membrane, may have great influence on the osmose. The double-membranes $\mid X \mid$ and $\mid Y \mid$ are viz.

both permeable for water of liquids of the field *W a m*;

both impermeable for water of liquids of the field *b d c*;
but $\mid X \mid$ is permeable and $\mid Y \mid$ is impermeable for water of liquids of the field *a m b d*.

When therefore, L_1 and L_2 represent, two liquids of the field *a m b d*, then system (17) remains unchanged, also when the two liquids are not isotonic, system (18), however, passes into an osmotic equilibrium.

If we take in the double-membrane a mixture of solid X and Y, then we have the osmotic system:

$$L_1 \overset{|}{\underset{|}{\rightarrow}} X + Y \overset{|}{\underset{|}{\leftarrow}} L_2 \quad \text{fig. 1 Comm. V.} \quad . \; . \; . \; . \quad (19)$$

in which the double-membrane is permeable for water from all liquids of the field *W b c a*.

As the O.W.A. of solid $X + Y$ is equal to that of liquid L_c and, therefore, greater than that of the liquids of the field *W b c a*, in (19) the water shall diffuse in the direction of the arrows. It now depends on the composition of the liquids L_1 and L_2 and on the ratio's of the quantities of $X\, Y\, L_1$ and L_2 which equilibrium shall be formed from (19). If we represent this by:

$$E_1 \mid D \mid E_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

then E_1 D and E_2 can be one of the equilibria:

$$X + Y + L_c\,, \quad X + L', \quad Y + L'' \text{ or } L''' \quad . \; . \; . \; . \quad (21)$$

Herein L' represents a liquid of the saturation-curve *b c*, L'' a liquid of the saturation-curve *a c* and L'' an unsaturated liquid.

System (20), therefore, can represent a.o. the osmotic equilibrium:

$$L_1 \mid L \mid L_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

in which three unsatured liquids, represented by points of an isotonic curve; it can represent also the osmotic equilibrium:

$$Y + L_e \mid L \mid X + L_f \quad \text{fig. 1 Comm. V} \; . \; . \; . \; . \quad (23)$$

liquid L then is situated on the isotonic surve *e f*. It can represent also an osmotic equilibrium:

$$X + L_g \mid L \mid X + L_g \text{ or } L \mid X + L_g \mid X + L_g \quad \text{fig. 1 Comm. V} \quad (24)$$

in which L is a liquid of the isotonic curve, going through point g. In each of the two osmotic equilibria (24) two identical liquids L_g occur; even it is possible that an osmotic equilibrium is formed with three identical liquids, f.i.

$$X + L_g \mid X + L_g \mid X + L_g \quad \text{fig. 1 Comm. V.} \quad . \; . \quad (25)$$

This is possible only then, when the liquids L_1 and L_2 of system (19) are situated both in the field Wbc and when the complex $X+Y$ o the double-membrane is represented by a point between X and c' (imagine c' to be the point of intersection of the side XY with the line Wc, which is not drawn).

In the osmotic system

$$L_1 \mid X \mid L_2 \quad \text{fig. 1 Comm. IX.} \quad \ldots\ldots \quad (26)$$

L_1 represents a liquid with the components $W+X+Y$ and L_2 with the components $W+X+Z$. Consequently liquid L_1 is situated in triangle WXY and L_2 in triangle WXZ of fig. 1 Comm. IX.

If L_1 is situated within the field Wdr_1 and L_2 within the field Wdr_2 then (26) passes into one of the osmotic equilibria:

$$L'_1 \mid L \mid L'_2 \ (27a) \quad L'_1 \mid X+L_d \mid L'_2 \quad \ldots\ldots \quad (27b)$$

When in (27*a*) L is represented f. i. by point q then L'_1 is situated on qq_1 and L'_2 on qq_2. When the double-membrane contains much solid X then the equilibrium (27*b*) is formed, L'_1 is situated then on curve dr_1 and L'_2 on curve dr_2.

The osmotic system

$$L_s \mid X \mid L_w \quad \text{fig. 1 Comm. IX} \quad \ldots\ldots \quad (28)$$

may pass into an osmotic equilibrium (27*a*) with three unsaturated isotonic liquids; it can form also one of the systems:

$$E = L_t \mid X+L_d \mid L_v \qquad K = L_t \mid X \mid L_u \quad \ldots\ldots \quad (29)$$

The first is an osmotic equilibrium; the latter is a complex in which L_u has a greater O.W.A. than L_t. The diffusion of water, however, is also prohibited by the double-membrane.

The reader may easily deduce the other cases, also when we use the double-membranes $\mid Y \mid$ or $\mid X+Y \mid$. I only wish to draw the attention to the fact that the double-membrane $\mid X \mid$ is impermeable for water from liquids of the fields dr_1ab and dr_2Zg, the double-membrane $\mid Y \mid$ for water from liquids of the fields acb and $ehZg$ and the double-membrane $\mid X+Y \mid$ for water from liquids of the field $fiZg$.

(*To be continued*).

Chemistry. — "*The fictitious heats of solution of enantiotropic modifications at their transition point*". By Prof. ERNST COHEN and Mr. H. L. BREDÉE.

(Communicated at the meeting of April 25, 1925).

Introduction.

1. In his "Recherches expérimentales et théoriques sur les Equilibres Chimiques" [1]) LE CHATELIER, a long time ago, has pointed at a highly interesting relation which must exist at the transition point of enantiotropic modifications. If we call these two modifications, which are in equilibrium with each other at the temperature of transition T_0, α and β, the temperature coefficients of the solubility at T_0 $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$, respectively, the fictitious heats of solution Q_α and Q_β, then, according to LE CHATELIER we have at T_0:

$$\frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta}=\frac{Q_\alpha}{Q_\beta} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

About this point LE CHATELIER observes: "Il serait intéressant de vérifier cette conséquence de la formule, qu'au point de transformation le rapport des tangentes est égal au rapport des chaleurs de dissolution:

$$\frac{\frac{dc}{dT}}{\frac{dc'}{dT}}=\frac{L}{L'}."$$

Only recently P. MONDAIN MONVAL [2]) has taken up the testing of this "Law of Tangents", choosing for his object those modifications of ammonium nitrate (the β-rhombic and the α-rhombic, which we shall indicate by the names of modification III and IV) which have their transition point [3]) at 32°.3 C. From his experiments he deduces:

$$\frac{Q_\alpha}{Q_\beta}=1.158; \quad \frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta}=1.17.$$

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[1]) Paris 1888; pag. 165.

[2]) C. R. Paris **177**, 175 (1923); Thèses, Paris 1924; Ann. de Chimie **3**, 72, 121 (1925).

[3]) ERNST COHEN and J. KOOY, These Proceedings **27**, 65 (1924); also Zeitschr. f. physik. Chemie **109**, 81 (1924).

Here he observes: „Si nous rapprochons les valeurs de ces rapports nous voyons que l'écart qui existe entre elles est d'environ 1 %. Cet accord excellent tient évidemment en partie à une heureuse coïncidence. En égard à la difficulté des mesures et à la précision respective avec laquelle elles ont été effectuées, un écart de 4 à 5 % n'aurait rien que d'acceptable", and his final conclusion is: „Les mesures que nous avons effectuées sur les modifications allotropiques du nitrate d'ammonium aux environs de 32° vérifient donc plus exactement qu'on ne pouvait l'espérer la loi du rapport des tangentes".

2. We cannot agree with this opinion. For, the agreement which MONDAIN MONVAL assumes from his measurements, does not really exist. It seems to exist, because he chooses quite arbitrary values out of his experimental data. Here again we have a case as is so often found in the literature, when we have to test thermodynamic relations. MOESVELD [1]) has already directed attention to this fact, and we wish to point out here, that it is of great importance to trace the cause of this non agreement, when it seems that there is a discrepancy between theory and experiment, as such an investigation often leads to the discovery of new phenomena. For instance, during our investigations on the metastability of matter [2]), new phenomena have been brought to light, and these could be studied quantitatively, because we chose for our starting-point the divergencies between calculation and experiment which had appeared, when the equation of CLAPEYRON-CLAUSIUS was applied to the modifications III and IV of ammonium nitrate.

3. While, in an investigation by COHEN and HELDERMAN [3]), the curves of the intermediate heats of solution of the two forms of ammonium nitrate mentioned, had been accurately determined, we have very carefully measured the values of $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$ at the transition temperature (32°.3 C.) in order to test the relation of LE CHATELIER. In the present paper we describe the investigation referring to it, and in conjunction with it, a discussion of the results of MONDAIN MONVAL.

A. The Materials used.

4. The ammonium nitrate which we used in our investigation was obtained by recrystallizing an already pure commercial preparation several times out of carefully distilled water. An analysis, to show the degree of purity finally attained was made, according to the method, described

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[1]) The Testing of BRAUN's Law, Utrecht 1918, page 7.

[2]) These Proceedings **27**, 65; **28**, 1 (1924); Zeitschr. f. physik. Chemie **109**, 81; **113**, 145 (1924).

[3]) These Proceedings **28**, 2 (1924); Zeitschr. f. physik. Chemie **113**, 145 (1924).

in KRAUCH "Die Prüfung der Chemischen Reagentien auf Reinheit" [1]). No impurities were found.

5. We have also ascertained the purity of our material by determining the solubility of crystals prepared by successive crystallizations, according to the method described hereafter. In this way a certain crystallization gave at 20°.00 the values of 65.24 and 65.24. Crystals of the next crystallization gave the values of 65.25; 65.24 and 65.26.

B. The solubility determinations.

1. *General observations.*

6. The greatly divergent values which are found in the literature for the solubility of ammonium nitrate at one and the same temperature [2]), prove already that it is very difficult to carry out reliable determinations for this highly soluble salt. For this reason we have taken very great pains with these measurements, and have succeeded in carrying out the determinations with an accuracy of 0.02 to 0.03 %, in which equilibrium was always reached, starting from unsaturated as well as supersaturated solutions. Great accuracy is required, as, when LE CHATELIER's equation is to be tested, it is just the point to fix the differential quotients, which from their very nature are very susceptible to slight errors in the values of solubility. All the determinations were carried out in triplicate, while the weighings (on a BUNGE balance, which allowed an accuracy of the weighings to 0.1 mgr.) were reduced to vacuum. Our weights were calibrated according to the well known method of F. KOHLRAUSCH. The thermometers used were compared with an instrument graduated in tenths of a degree, and calibrated by the Physikalisch-Technische Reichsanstalt at Charlottenburg, the zero point of which we have controlled. In our thermostats, in which the equilibrium of solution was attained by shaking water with excess of salt, was always a BECKMANN thermometer, divided into hundredths of a degree. The regulation of the temperature was brought about by a regulator according to OSTWALD (capacity of the bulb about 500 cc), which we filled with tetrachlorethane, a liquid which has the advantage over toluene in being non-inflammable, which is very convenient when filling the bulb. The time of shaking varied between 4 and 48 hours. The temperature variations of the thermostat during a short period were not greater than 0.01 degree, at 5° and 10° two hundredths of a degree at most. The shaking of the solutions in the thermostat was done by means of the acatène-apparatus, which has been described by COHEN and BRUINS in a former paper [3]).

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[1]) Berlin, 1896. Dritte Auflage, S. 32.

[2]) A synopsis is found in MONDAIN MONVAL. See note 2 page 377.

[3]) Zeitschr. f. physik. Chemie **93**, 43 (1918).

7. In the analysis of the saturated solutions, which, also at the higher temperatures, had to be carried out without loss of liquid (owing to evaporation) the method was followed which had been indicated by COHEN and MOESVELD [1]): the curve was determined which represents the specific volume of aqueous solutions of ammonium nitrate as function of the concentration (at a definite temperature). The concentration of the saturated solutions is then found by determining their specific volume (at the temperature for which the curve mentioned has been fixed) and by calculating the concentration from the equation which represents the relation between specific volume and concentration.

8. As the temperature coefficient of the solubility of ammonium nitrate is very great, the pyknometer, into which the saturated solution is pressed, must, during this manipulation, be totally immersed in the thermostat in which equilibrium of solution is reached. For particulars of this technique we refer to the paper by ERNST COHEN, WILHELMA A. T. DE MEESTER and A. L. TH. MOESVELD [2]) on the influence of pressure on the solubility of substances V, especially par. 11.

2. *The determination of the solubility of Ammonium nitrate IV.*

9. The range of stability of modification IV lies [3]) between — 16° and + 32°.3 C.

Our determinations of solubility have been carried out at 0°.00; 5°.00; 10°.00; 15°.00; 20°.00; 25°.00; 30°.00 and 32°.00 C.

In order to determine the concentration of saturated solutions between 0° and 32°.3 C. we might actually have used the equation previously found by COHEN, HELDERMAN and MOESVELD [4]), which represents the relation between specific volume and concentration of solutions of ammonium nitrate at 32°.3 C.:

$$(v_c)_{32^\circ.3} = 1.00507 - 0.00392087\,c + 0.0000051003\,c^2 - 0.00000000566\,c^3. \quad (2)$$

Meanwhile we have again determined this relation.

10. For this purpose we prepared solutions of accurately known concentration by weighing (in flasks, similar to those which were used for the determinations of solubility) salt (which had been strongly dried under particular precautions which have previously been described [5]) and water

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[1]) Zeitschr. f. physik. Chemie **94**, 482 (1920).

[2]) These Proceedings **28**, 108 (1924); also Zeitschr. f. physik. Chemie **114**, 321 (1924).

[3]) ERNST COHEN and J. KOOY, These Proceedings **27**, 65 (1924); also Zeitschr. f. physik. Chemie **109**, 81 (1924).

[4]) See these Proceedings **27**, 565 (1924), especially par. 9. Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

[5]) See these Proceedings **27**, 565 (1924). Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

the specific volume of these solutions was then determined at 32°.3 C. in the way described in par. 8. Great care was taken that no evaporation could take place during the solving of the salt, which was brought about by heating: the flasks were closed during the heating.

The results thus obtained are given in table 1.

TABLE 1.

Temperature 32°.3 C.

Concentration in gr. per 100 gr. of solution	Spec. vol. found C. and B.	Spec. vol. calculated C. and B. equation (3)	Spec. vol. calculated C. H. and M. equation (2)
25.00	0.91012	0.91011	0.91015
34.99	0.87377	0.87375	0.87387
44.98	0.83829	0.83830	0.83850
54.98	0.80374	0.80372	0.80398
64.98	0.77003	0.77002	0.77028
70.65	0.75125	0.75129	0.75152

According to the method of least squares we find from the values in the first and second columns:

$$(v_c)_{32^\circ.3} = 1.00529 - 0.00392915c + 0.0000049640c^2 - 0.0000000333c^3. \quad (3)$$

From the second and third columns of table 1 we see that this equation describes the observations. Further we observe that the differences in concentration which the equations (2) and (3) yield for a given specific volume, attain at most an amount of 0.08 per cent.

11. The results of the solubility determinations of modification IV are summarized in table 2. By means of the method of least squares we find from it for $c_{IV} = f(t)$:

$$c_{IV} = 54.241 + 0.6106\,t - 0.00297\,t^2 \quad . \; . \; . \; . \; . \; . \quad (4)$$

Columns 6, 7 and 8 of table 2 prove that this equation holds good.

3. *The determination of the solubility of Ammonium nitrate III.*

12. The range of stability of this modification (III) lies between 32°.3 and 84°.2 C. Our solubility determinations within this range have been made at 33°.00; 36°.00; 39°.00; 42°.00; 45°.00 and 48°.00 C.

The curve which represents the specific volumes of solutions of ammonium nitrate as function of the concentration, has been fixed for

TABLE 2.

Solubility of Ammonium nitrate, Modification IV, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility; gr. of salt per 100 gr. of solution			$c_{calc.} - c_{found}$
				found from v_c	mean found	calculated	
0°.00	5½	0.80630	0.80629	54.23	54.23	54.24	+ 0.01
	4½	0.80627 *)		54.24			
	4½	0.80630 *)		54.23			
5°.00	4	0.79605 *)	0.79605	57.23	57.23	57.22	— 0.01
	5	0.79608		57.22			
	5	0.79603		57.24			
10°.00	4½	0.78656 *)	0.78651	60.04	60.05	60.05	± 0.00
	5	0.78650		60.06			
	5½	0.78646		60.07			
15°.00	4½	0.77740 *)	0.77741	62.77	62.76	62.73	— 0.03
	5½	0.77738		62.77			
	5½	0.77745		62.75			
20°.00	4	0.76917 *)	0.76914	65.24	65.24	65.27	+ 0.03
	4	0.76916 *)		65.24			
	24	0.76910		65.26			
	4	0.76912 *)		65.25			
	48	0.76914		65.24			
25°.00	24	0.76123	0.76122	67.63	67.63	67.65	+ 0.02
	24	0,76118		67.64			
	5	0.76125 *)		67.62			
30°.00	24	0.75375	0.75374	69.90	69.90	69.89	— 0.01
	24	0.75377		69.89			
	5	0.75370 *)		69.91			
32°.00	24	0.75087	0.75090	70.78	70.77	70.74	— 0.03
	24	0.75090		70.77			
	24	0.75092		70.76			

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*) signifies: starting from supersaturated solution.

50°.00 C. so that the saturated solutions which were formed at the highest temperature investigated (48°) could never crystallize during the determination of their specific volume.

The equation of the curve $(v_c)_{50^\circ 00} = f(c)$ was obtained by determining the specific volume at 50° of solutions which contained 15, 25, 35, 45, 55, and 75 % of salt respectively (sum = 100), and which had been prepared by weighing, as is described in par. 10. Table 3 contains the results of the determinations of the specific volume.

TABLE 3.

Specific Volume of Ammonium nitrate solutions of different concentrations.

Temp. 50°.00 C.

Weight of salt in grms	Weight of solution in grms	Concentration grms of salt in 100 gr. of sol.	v_c found	v_c mean found	v_c calc.	v_c calc.-found $\times 10^5$
5.1247	34.1904	14.99	0.95527	0.95525	0.95532	+ 7
5.1247	34.1904	14.99	0.95522			
10.8391	43.3554	25.00	0.91826	0.91828	0.91822	— 6
10.8391	43.3554	25.00	0.91830			
15.1917	43.4148	34.99	0.88206	0.88207	0.88192	— 15
15.1917	43.4148	34.99	0.88208			
19.9609	44.3810	44.98	0.84626	0.84630	0.84631	+ 1
19.9609	44.3810	44.98	0.84634			
24.9593	45.3964	54.98	0.81123	0.81122	0.81136	+ 14
24.9593	45.3964	54.98	0.81120			
28.4039	43.7149	64.98	0.77708	0.77710	0.77708	— 2
28.4039	43.7149	64.98	0.77712			
32.1572	42.8859	74.99	0.74346	0.74348	0.74341	— 7
32.1572	42.8859	74.99	0.74350			

By means of the method of least squares we find:

$$(v_c)_{50^\circ.00} = 1.01227 - 0.0038565\,c + 0.000003855\,c^2 - 0.00000000319\,c^3. \quad (5)$$

From columns 5, 6 and 7 of table 3 we see that the equation describes the experimental data.

13. We have also controlled the equations (3) and (5) mutually, by determining the specific volume of the solution, saturated at 32°.3, at that temperature as well as at 50°.00 C, and by deducing from it the concentration of the solution by means of the equations (3) and (5).

In this way we found from the determinations of the specific volume at 32°.3 C. the values 70.87
and 70.88
and from the determinations of the spec. vol. at 50°.00 C. the values 70.87
and 70.86,
in other words: complete agreement.

14. As regards the determinations of solubility of modification III itself may be observed that they were done in the very same way as those of modification IV. The results are found in table 4. By means of the method of least squares we find for $c_{III} = f(t)$:

$$c_{III} = 57.861 + 0.4384\, t - 0.00111\, t^2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From columns 6, 7 and 8 of table 4 we see that this equation describes the observations.

C. Calculation of the Transition temperature.

15. The point of intersection of the curves, represented by the equations (4) and (6) gives for the transition temperature

$$t = 32°.27 \text{ C.}$$

while $c_{IV} = c_{III} = 70.85$.

So there is complete agreement between this result and the fact that COHEN and KOOY [1]) have found the temperature of transition $IV \rightleftarrows III$ at 32°.3 C. We wish, however, to observe that too great a value must not be attached to this agreement, as for $t = 31°.8$ or 32°.8 the two equations give a difference in the solubility of only 0.025 per cent, a difference which lies within the errors of the measurements.

D. Calculation of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ at the Transition temperature.

16. If we call the values

$$\left(\frac{dc}{dT}\right) \text{and} \left(\frac{dc'}{dT}\right),\ L \text{ and } L'$$

from LE CHATELIER's equation (see above par. 1) in our case, where they refer to the modifications IV and III of ammonium nitrate $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$, respectively Q_{IV} and Q_{III}, we find:

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[1]) These Proceedings **27**, 65 (1924); Zeitschr. f. physik. Chemie **109**, 81 (1924).

TABLE 4.

Solubility of Ammonium nitrate, Modification III, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility; gr. of salt per 100 gr. of solution			$c_{calc.} - c_{found}$
				c_{found} fr. v_c	c mean found	c calculated	
33°.00	15	0.75638 *)	0.75636	71.11	71.12	71.12	± 0.00
	18	0.75636		71.12			
	18	0.75635		71.12			
36°.00	12	0.75268 *)	0.75271	72.22	72.21	72.20	— 0.01
	18	0.75272		72.20			
	18	0.75272		72.20			
39°.00	12	0.74915 *)	0.74914	73.27	73.27	73.27	± 0.00
	18	0.74913		73.28			
	18	0.74913		73.28			
42°.00	12	0.74564 *)	0.74563	74.32	74.32	74.32	± 0.00
	18	0.74563		74.32			
	18	0.74562		74.33			
45°.00	4	0.74222 *)	0.74223	75.35	75.34	75.34	± 0.00
	5	0.74225		75.34			
	5	0.74223		75.34			
48°.00	12	0.73885 *)	0.73886	76.36	76.35	76.34	— 0.01
	24	0.73887		76.35			
	24	0.73887		76.35			

*) signifies: starting from supersaturated solution.

From equation (4):

$$\left(\frac{dc}{dT}\right)_{IV} = 0.6106 - 2 \times 0.00297 \times 32.27 = 0.4189 \; \frac{\textit{weight}\ {}^0/_0}{\textit{degree}}.$$

From equation (6):

$$\left(\frac{dc}{dT}\right)_{III} = 0.4384 - 2 \times 0.00111 \times 32.27 = 0.3668 \; \frac{\textit{weight}\ {}^0/_0}{\textit{degree}};$$

therefore

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}}=\frac{0.4189}{0.3668}=\mathbf{1.14^2}\,.$$

E. Calculation of $\frac{Q_{IV}}{Q_{III}}$ *at the Transition temperature.*

17. By means of an adiabatic, electrical method for the intermediate heats of solution of modification IV and III at their point of transition (32°.3) ERNST COHEN and W. D. HELDERMAN [1]) have found:

$$(Q_i)_{IV}=-5910+83.057\,c-0.73476\,c^2+0.00224\,c^3\,. \quad . \quad . \quad (7)$$

and

$$(Q_i)_{III}=-5510+83.057\,c_1-0.73476\,c_1^2+0.00224\,c_1^3 \quad . \quad . \quad (8)$$

in which c, respectively c_1, represents the concentration of a solution of ammonium nitrate (sum $=100$), in which one molecule of the modification in question is dissolved.

For the transition temperature [2]) $c=c_1=70.93$; by means of the equations (7) and (8) we then find:

$$Q_{IV}=-2917 \text{ gramcalories}$$

and

$$Q_{III}=-2517 \text{ gramcalories}$$

so:

$$\frac{Q_{IV}}{Q_{III}}=\frac{2917}{2517}=\mathbf{1.15^9}\,.$$

F. Experimental proof of the relation of LE CHATELIER.

18. Whereas in par. 16 was found:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}}=\mathbf{1.14^2}$$

we find in par. 17

$$\frac{Q_{IV}}{Q_{III}}=\mathbf{1.15^9}$$

which proves experimentally the exactness of LE CHATELIER's relation.

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[1]) These Proceedings **28**, 1 (1924); Zeitschr. f. physik. Chemie **113**, 145 (1924).

[2]) We take here 32°.27 C., the point of intersection of the curves of solubility, therefore the value which was found in par. 15, instead of 32°.3, the value determined by COHEN and KOOY by dilatometric way.

G. MONDAIN MONVAL's *investigation.*

1. *The solubility determinations.*

19. The results of his solubility determinations are given in table 5

TABLE 5.

Solubility of NH_4NO_3 at different temperatures (MONDAIN MONVAL).

Temperature	Gr. NH_4NO_3 in 100 gr. of water	Molecular concentration C. (sum = 1)
26°.7	215.0	0.3257
28.6	223.6	0.3344
29.4	227.1	0.3379
30.4	232.5	0.3431
30.8	234.5	0.3450
32.2	241.2	0.3515
32.9	244.4	0.3544
33.8	248.3	0.3581
35.3	255.6	0.3648
36.0	259.0	0.3679
39.2	274.5	0.3814

By means of these experimental results, which give a point of intersection of the solubility curves of modification IV and III at 31°.8 MONDAIN MONVAL calculates (without further explanation) for the quotient

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}}$$ the value of 1.17, at the temperature mentioned.

By means of the method of least squares we find, however, from columns 1 and 3 in table 5:

$$c_{IV} = 0.3354 + 0.00472\,(t - 28.8) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$c_{III} = 0.3664 + 0.00429\,(t - 35.7) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Table 6 proves that the equations (9) and (10) are in very close agreement with the results of MONDAIN MONVAL.

TABLE 6.

Temperature	c_{found}	$c_{calculated}$	$(c_{calc.} - c_{found}) \times 10^4$
26°.7	0.3257	0.3255	— 2
28.6	0.3344	0.3345	+ 1
29.4	0.3379	0.3382	+ 3
30.4	0.3431	0.3430	— 1
30.8	0.3450	0.3448	— 2
31.8	0.3500	0.3496	— 4
32.2	0.3515	0.3514	— 1
32.9	0.3544	0.3544	± 0
33.8	0.3581	0.3582	+ 1
35.3	0.3648	0.3647	— 1
36.0	0.3679	0.3677	— 2
39.2	0.3814	0.3815	+ 1

The point of intersection of the curves (9) and (10) is 31°.8, while, by means of these equations we find:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = \frac{0.00472}{0.00429} = 1.10$$

and *not* 1.17, which figure is given by MONDAIN MONVAL.

20. We are of opinion that it is superfluous to trace the reason which has led to such a great divergence from the figure (1.14) found by us. We only wish to observe that MONDAIN MONVAL finds values for the solubility at all the temperatures investigated by him, which lie far below ours, and as we have always attained equilibrium of solution with highly different periods of shaking, from above as well as from below, at which we found identical values, whereas he, with far shorter periods of shaking (during which the temperature was but a short time above the temperature of equilibrium) thought to have reached equilibrium, it is very probable that in his investigations this has not been the case.

The way in which MONDAIN MONVAL prepares the saturated solutions for analysis (filtering the excess of salt through a previously heated funnel, during which crystallisation is not excluded) may also have been one of the causes of his too low results. Then he has been experimenting within too small ranges of temperature, so that the values of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ are doubtful.

2. *Determination of the fictitious heats of solution* Q_{IV} and Q_{III}.

21. Now that we have obtained *our* results we will not enter into a discussion of the particulars of MONDAIN MONVAL's method to find $\frac{Q_{IV}}{Q_{III}}$, and only wish to observe, that the way, in which he has measured the intermediate heats of solution of the two modifications in solutions of different concentrations, has been a rather rough one. COHEN and HELDERMAN [1]) have determined those values by means of a highly perfected, calorimetric method, with an accuracy of 0.3 per cent. Tables 7 and 8 show that the divergencies between the values of MONDAIN MONVAL and those of COHEN and HELDERMAN are not inconsiderable.

MONDAIN MONVAL calculates the quotient $\frac{Q_{IV}}{Q_{III}}$ by means of the values found by him $Q_{IV} = -2.93$ and $Q_{III} = -2.53$, whereas the investigation by COHEN and HELDERMAN has given the values -2.91^7 and -2.51^7. The value of $\frac{Q_{IV}}{Q_{III}}$, calculated by MONDAIN MONVAL happens to be the same as the value furnished by the much more accurate figures of COHEN and HELDERMAN, viz. 1.16.

TABLE 7.

Intermediate heats of solution of Ammonium nitrate, Modification IV, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 28° and 32°.3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN—HELDERMAN	
1	0	2.23	1.11	— 5.90	— 5.819	+ 0.08
2	20	22.03	21.01	— 4.62	— 4.468	+ 0.15
3	50	50.91	50.46	— 3.33	— 3.302	+ 0.03
4	56.9	57.53	57.22	— 3.19	— 3.144	+ 0.05
5	66.6	67.18	66.89	— 3.02	— 2.972	+ 0.05

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[1]) These Proceedings **28**, 1 (1924); Zeitschr. f. physik. Chemie **113**, 145 (1924).

TABLE 8.

Intermediate heats of solution of Ammonium nitrate, Modification III, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 36° and 32°.3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN—HELDERMAN	
1	0	2.57	1.28	— 5.35	— 5.405	— 0.06
2	34.8	35.94	35.37	— 3.44	— 3.392	+ 0.05
3	57.0	57.71	57.36	— 2.86	— 2.741	+ 0.12
4	70.0	70.37	70.19	— 2.54	— 2.525	— 0.01

22. From the investigation of MONDAIN MONVAL results:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = 1.10 \quad \text{en} \quad \frac{Q_{IV}}{Q_{III}} = 1.16.$$

A satisfactory experimental testing of the "law of tangents" is therefore out of the question.

Summary.

In the above paper was shown that the experimental testing of the "Law of Tangents" of LE CHATELIER by MONDAIN MONVAL has led to unsatisfactory results, in consequence of insufficient accuracy of the data necessary for such a proof. An agreement between theory and experiment, satisfactory in every respect, was found by employing more accurate methods.

Utrecht, April 1925. VAN 'T HOFF *Laboratory.*

Geology. — *"The Palaeothermal Problem in the Light of the Giant and Dwarf Theory of Stellar Evolution"*. By Prof. Eug. Dubois.

(Communicated at the meeting of May 30, 1925).

In all geographical formations with well characterized faunas or floras, starting with the Cambrium, these up to the upper division of the Tertiary give evidence of a hotter climate than at present, pliothermal conditions, at high geographical latitude. Though the distribution over the Earth was never perfectly uniform, it is not until the beginning of the Tertiary era, and then at first locally restricted, gradually more circumpolarly, that palaeontologic witnesses appear, testifying to gradual and progressing cooling, till at last in the Plistocene period evidence is found of the present distribution of heat.

Some of the surest palaeontological proofs of a hotter climate at high geographical latitude and more uniform distribution of heat over the Earth may be mentioned here, with a view to defining the palaeothermal problem.

In the Cambrian reef-building corals, which anthozoa now-a-days scarcely reach further than beyond the 28th degree of latitude at a single point, because they are physiologically-chemically restricted to hot seas, the secretion of lime being actually a function of the temperature, are met with up to 76° $^{1}/_{2}$ N. lat. in the New-Siberian Islands, and as far as beyond the Antarctic circle in Antarctica (Weddell-Sea).

Especially in the Upper Silurian formation coral reefs are known of all latitudes; in the extreme North, of the peninsula of Kanin, at 68° N. lat., and of the New-Siberian Islands and the Arctic-American Island of North-Devon, at 75° N. lat. The general hot climate throughout the period appears moreover from the cosmopolitan character of the faunas. In the Southern Hemisphere the Graptoliths in the South-Orkney Islands, found at 61° S. lat., bear witness to the same fact.

Also in the Devonian formation reef corals are found inside the Artic circle. The Upper Devonian floras of Ellesmere Land as well as of Bear Island at 78° N. lat. give evidence of the great uniformity of the vegetable world of the time. Likewise the marine Devonian fauna of the Falkland Islands and the Cape show the more uniform distribution of heat.

That the luxuriant Carboniferous flora, which is very uniformly of character over the whole Earth, must be considered as a lowland flora of a moist warm, i.e. tropical climate, appears beyond all doubt. In Spitsbergen reef corals are found in the Upper Carboniferous (chronologically equivalent to our coal-measures), and in the Lower Carboniferous of this group of islands and of Greenland, here even at 81° N. lat., the same flora as was widely spread at much lower latitude.

The Permo-Carboniferous Glossopteris flora of the Southern continents and India, which was found at 51° S. lat. as far as the Falkland islands, and in the Antarctic continent at 85° S. lat., i.e. five degrees from the pole, but also in Mongolia and China, and mixed with the northernhemispheric Permian flora, in Siberia and North Russia (at 61° N. lat.), had likewise the character of a flora of a hot and humid climate, as was recently set forth by GOTHAN [1]). This may also be derived from the fact that it occurs mixed with the Lepidodendron flora in South America and South Africa.

In the Triassic formation of Alaska the same fauna of reef-corals occurs at 60° N. lat. as in California at 41° 1/2 N. lat., and in the Alps up to 45° N. lat.

Among the most reliable palaeontological evidences of a tropical climate are large forms of Reptiles. As cold-blooded animals the Reptiles are entirely dependent on the temperature of their surroundings as regards metabolism and consequently in all their functions. For this reason their life is minimum in our winter; in recent times only small forms, which can hibernate hidden, can exist at high geographical latitude. The general presence at high geographical latitudes of large Theromorpha in the Upper Carboniferous, the Permian and the Triassic formation, of large Dinosauria throughout the Mesozoic era, from the Triassic up to the upper Cretaceous formation, prove with perfect certainty that the climate there was without any winter, i.e. tropical.

In the Permian period there lived in Russia, at 61° N. lat., large Theromorpha (Pareiasaurus, Inostranzewia and others) which were closely related to South African forms, belonging to a widely-spread fauna found also in India, Europe and North America up to the Triassic period.

To a hot climate at high geographical latitude point also the large Stegocephalic Amphibia in the Triassic formation of Spitsbergen.

Already in the Triassic period there existed large forms of Dinosauria in North America up to at least 43° N. lat., in Europe up to at least 53° N. lat., in South Africa, India, Australia. Large Dinosauria also occur in the Jurassic formation of North America, Europe, South Africa. The time at which these landreptiles really flourished is, however, the Cretaceous period. From the beginning till the end of this period there existed the rich fauna of gigantic Dinosauria in North America and East Africa, in India, Central Asia, and Europe, as well as in South America and Australia. We know it of 51° N. lat. in Canada, of 70° N. lat. in Greenland, of 51° N. lat. in Belgium,, of 45° N. lat. in Mongolia, and of 39° S. lat. in North Patagonia. That of East Africa (Tendaguru), at 10° S. lat., presents close resemblance to the famous fauna of the Como beds of North America. Compare Kentrurosaurus with Stegosaurus!.

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[1]) W. GOTHAN, Palaeobiologische Betrachtungen über die fossile Pflanzenwelt. Berlin 1924.

The flora of the Jurassic is more uniform than that of any other period. On the east coast of Greenland, at 70° N. lat., it had the same tropical or sub-tropical character as in England at 54° N. lat., and of the species of Ferns, Equisetaceae and Cycadeae found in West Antarctica at 63° 15′ S. lat., at least as many occurred also in Europe as in India.

Also the angiospermian Cretaceous flora of the west coast of Greenland had a sub-tropical character at 70° $^1/_2$ N. lat.; it shows to be allied to the Dakota-flora of western North America known to beyond 56° N. lat., which for the greater part resembled the hot-temperate angiospermian Cretaceous flora of South Patagonia at 51° S. lat.

Coral reefs of the Jurassic period are known in Europe up to 52° N. lat., in North America to 38° N. lat., and in South America to 40° S. lat. Those of the Cretaceous formation reach 47° $^1/_2$ N. lat. in Europe.

Important indications of a formerly hot climate are also given by fossil Palms. The general boundary lines of the present palm zone do not extend further than 38° N. lat. and 32° S. lat.; only a single palm species in the Pacific islands is found as far as 45° distant from the equator. The Middle Eocene flora of South England at 51° N. lat. contains a number of palm species. This flora presented on the whole, according to GARDNER, the appearance of the forests in the Malay Archipelago and tropical South America. The Middle Eocene flora of North America at the same latitude gives evidence of a much less hot climate than there. It contains but few palms, a deviation of the same nature as in the present temperatures of those places. At present the average temperature there in North America is in January 15° C. and in July 6° lower than in South England. The Eocene nummulites, which bear witness to the presence of hot sea-water, reached Zeeland in Holland, South England and even Bremen (53° N. lat.). The Eocene marine flora of Alaska (at about ten degrees higher latitude) was, indeed, only subtropical. In the Oligocene period coral reefs lay off the north and the south borders of the Alps, and as late as the Lower Miocene the tree flora of Europe contains some palm species by the side of a diminished number of other tropical forms to beyond 50° N. lat.

On the Pacific coast of North America, from Oregon northwards, only a cool-temperate climate prevailed in Miocene times. This difference in temperature between North America and Europe compared with the Arctic regions, which is constantly met with, corresponds to the present distribution of heat, and unless a consequence of a more America-ward position of the North Pole, it might be caused, just as at present, by hot North Atlantic ocean currents, which, undoubtedly, had preponderating influence in the Pliocene period.

The Arctic Tertiary floras, famous by the work of HEER, and now almost universally placed in the Eocene, have already long been considered of great significance for the palaeothermal problem. The most northern finding places are Grinnell land at 81° 45′ N. lat. and Spitzbergen at 78° 56′ N. lat. The richest finding-place lies on the west coast of Greenland, at 70° N. lat. Such floras of from uniformly temperate to a hot-temperate climatic character are now-a-days found 20 to 30 degrees more south. An equally mild climate as that of Greenland at 70° N. lat. must have been that in which existed the Eocene flora of Alaska between 55° and 62° N. lat. On the other hand, judging from the fossil flora, the Miocene climate of Japan, at about 33° N. lat., was slightly cooler than its present climate. But this seems to be compatible with a circumpolar hot condition, when by strengthening of the hot North Atlantic ocean-currents, the Arctic lowlands, especially in winter, were favoured, and Japan, in consequence of a more pronounced monsoon climate, in winter, was in a less favourable condition as regards heat.

In the Southern Hemisphere the fossil flora of Coronel in Chili, which is Lower Miocene or older according to Berry, bears the character at 37° S. lat. of a tropical rain-wood flora. At present the temperature is there on an average 15° C. in January and 10° C. in July. The Eocene flora of the northern island of New Zealand, at about the same latitude, is described as only temperately-subtropical. The present temperature is there almost 20° C. in January and 10° in July. The formerly more favourable thermal condition on the coast of Chili than in New Zealand may probably be explained by the at the time less cold polar current along this coast, as a necessary consequence of a general pliothermal condition. The so-called Fagus flora of the region round the Strait of Magellan, between 51° and 53$^{1}/_{2}$° S. lat., which was hesitatingly placed in the Lower Miocene by DUSÉN, suggests a formerly hot-temperate, and in opposition to the present, a humid climate. In our times it is much cooler there, the average temperatures being 10° C. in January and 5° C. in July. Of the highest southern latitude is the fossil flora of Seymour-island in West Antarctica, at 64°15′ S. a place now buried under ice, which flora was placed in the Tertiary by DUSÉN. It gives evidence of a subtropical climate. These South-American and Antarctic floras are considered as Plistocene by IRMSCHER [1]) in connection with the hypothetical place of the pole according to WEGENER. The subtropical Seymour flora then remains, however, at at least 50° S. lat. WEGENER himself places it at 45° S. lat. in the Upper Tertiary. If the indeed not sharp, but at any rate older estimations of the geological age of these floras by BERRY and DUSÉN are accepted, they fit into the frame of the Tertiary floras of the Northern Hemisphere, which bear witness to a hotter condition throughout the

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[1]) E. IRMSCHER, Pflanzenverbreitung und Entwicklung der Kontinente. Hamburg 1922

Boreal Earth, with temperatures diminishing from the beginning to the end of the Tertiary era. Disturbances in the zonic climate system, as in Europe through hot ocean-currents, in Japan through the monsoon-climate could locally retard or accelerate the, on the whole gradual, cooling, in the former case cause the temperatures even to rise above the earlier ones, in the latter case cause them to fall below the present ones. To the latter the Miocene glacial deposits in Alaska seem also to testify.

Of the orders of Reptiles extant after the Mesozoic era large forms are now-a-days found only in hot climates, at low geographical latitude. In the Tertiary of Europe Crocodiles and large Tortoises — not seldom of genera identical with those living at present — and also large Snakes are met with at high latitude. Thus Tomistoma, the Malay Gavial, up to 48°10′ N. lat. in the Miocene of Lower Austria, a gigantic Testudo as far as $42^{\circ 1}/_{2}$ N. lat. in the Pliocene of South France, large Pythonides in the Eocene of England, Belgium, France, Switzerland. In North America, on the other hand, Alligator is found only 5 degrees more northern than at present, in the Lower Pliocene of Nebraska, a little above 40° N. lat.

In the Miocene of Central France (Allier) a Parrot was found of the present tropical African genus Psittacus.

Anthropoid Apes are found in the Miocene and earliest Pliocene of Europe. The best-known are the large Dryopithecus and the small Pliopithecus. Dryopithecus was found in the south and the south-east regions of France up to $45^{\circ 1}/_{2}$ N. lat., also in Spain, on the southside of the Pyrenees at 42°20′ N. lat., in Upper-Swabia at 48° N. lat. and with Pliohylobates in Rhine-Hessen at 49°40′ N. lat. Pliopithecus is known from south, south-east and central France up to 48° N. lat., from northern Switzerland ad $47^{\circ 1}/_{2}$ N. lat., from Upper-Swabia at $48^{\circ 1}/_{2}$ N. lat., from Styria at $47^{\circ 1}/_{2}$ N. lat., and from Silesia (Oppeln) at 50°40′ N. lat. As all present-day Anthropoid Apes are confined to the tropical rain-wood zone, the small forms (the Hylobatides) are met with only at a latitude 25° degrees lower in Burma, and the large forms in Sumatra, Borneo, and in Africa are found only to 5 degrees distant from the equator, it may be assumed that the Miocene and Old Pliocene climatic condition in the regions of Europe agreed with that in the present tropical rain-wood zone. Certainly the occurrence of a number of large Anthropoid Apes, among others Dryopithecus-species, in the Siwalik beds of the same time, to 33° N. lat., point to a climatic condition as is now-a-days to be found only at a few degrees' distance from the equator. The same may be said of the South African Australopithecus, which was found at a distance from the equator 23 degrees larger than the Gorilla and Chimpanzee of these times, to which this fossil, probably Lower Plistocene Anthropoid Ape is certainly closely allied.

Homunculus, an Ape of the family of the Cebidae, which family is now-a-days confined to the tropical rain-wood zone of America, was found in the Upper Miocene of Patagonia, at 50° S. lat., hence its testimony goes to prove the same.

Of the family of the Cynopithecidae only a single species hardly reaches, under particularly favourable circumstances (in Japan), the 41st degree of latitude, but in the Lower Plistocene (or Upper Pliocene) of Europe representatives of this family are found in different places of higher geographical latitude (in South France, Hungary, Wurtemberg, England). The most northern finding-places are the Heppenloch at Kirchheim in Wurtemberg, at 48 40′ N. lat., and the Cromer Forest-Bed, at 52° $^{1}/_{2}$ N. lat. In those times Hippopotamus in Europe was found to beyond the 50th degree of latitude (Cromer, Tegelen), 20 degrees more to the north than it lived in historical times (in the Nile delta and the Jordan valley).

In the same way the Lower Interglacial fauna and flora of Tegelen, which may be referred to the upper Pliocene, at 51° 20′ N. lat., and the rich Megalonyx-fauna, which is met with in the Lowest-, Pliocene or Aftonian Interglacial of North America, to 41° N. lat., testify to warm-temperate, humid climates.

After this time it has never been considerably hotter anywhere at higher geographical latitude, than at present. It had generally become so much cooler here that with slight intermittant fall of the temperature, which also manifests itself in earlier formations, glacial periods could now begin to interchange with interglacial -times. Before the Upper Pliocene, unless it be in the Miocene of Alaska and possibly Northeast Siberia, no traces of such an alternation of glacial and interglacial periods with comparatively small differences of temperature, are found, evidently because then it was still too hot on our planet for this.

To this short enumeration of some of the surest palaeontological proofs of a formerly warmer climate at high geographical latitude a geological testimony may be added, i.e. the occurrence in old formations of such products of weathering as laterite and beauxite. The Plistocene or older laterite in the Kalahari of South Africa, probably also the laterite of West Australia, the Cretaceous beauxite of South France, the Pliocene of the Vogelsberg in Germany and the Eocene of Antrim in Ireland testify, like the beauxite of Alabama in North America, to a former tropical climate.

Of equally great significance in the palaeothermal problem as the palaeontological proofs of former hotter conditions at high geographical latitude are the geological proofs of former cold conditions at comparatively low geographical latitude, the palaeozoic and proterozoic ground moraines or tillites. We know most about the Permo-Carboniferous "Ice Age", the glaciation of South Africa, India, Australia, and South America which took place at the transition of the Carboniferous in the Permian period. This glaciation has been proved with as much certainty — especially through polished and striated rocks under the tillites which, shown by MOLENGRAAFF in South Africa for the first time with certainty, have now been found everywhere — as the Plistocene glaciation of Europe and North America, South America, Australia, Tasmania and New-Zealand. In some places viz. in New South Wales and West Australia, in North India and South West Africa, glacial deposits were formed in the sea by floating ice.

In South Africa the traces of this Permo-Carboniferous "Ice Age" are found from 33° 1/2 S. lat., in Cape Colony, to 8° S. lat., in Katanga [1]); in India from 20° N. lat., in Central India, to 32° 1/2 N. lat., in the Salt Range; in Australia from 21° S. lat., in Queensland, to 43° S. lat., in Tasmania; in South America from 23° S. lat., in Brazil, to 52° S. lat., in the Falkland Islands.

The great prevalence of its ground-moraines does *not* distinguish the Permo-Carboniferous glaciation from the Plistocene, for this extended in the Cordilleras of South and Central America over 70 degrees of latitude and in fact over all the continents at the same time. But in contrast to the Plistocene the Permo-Carboniferous glaciation seems to have no *bipolar character*, for in the Northern Hemisphere unmistakable and extensive Permo-Carboniferous traces of ice have not been found except at comparatively low latitude, only in and near India. At any rate the extension in the Northern Hemisphere was comparatively restricted. Nor is a shift of the pole conceivable with the present situation of the continents, through which bipolarity of the known Permo-Carboniferous ice-traces would be obtained. Besides the general direction of the movement of the ice-sheets in South Africa is towards the South pole, in Australia and India away from the pole, hence at least partly *independent* also of the South pole, even if its position had been different.

It is further in contrast to the Plistocene glaciation that most traces of the Permo-Carboniferous ice age occur at comparatively low latitude; even the marine glacial deposits are found at only about 33°, in India north of the equator and in Australia south of the equator, and at 27° S. also in South Africa.

Still in another respect does the Permo-Carboniferous glaciation greatly differ from the Plistocene, i.e. in this that the climatic character of the fossil flora immediately under and above the tillite and where two successive ground-moraines are found, in New South Wales, also that of the interglacial flora, presents more or less a tropical hot, not only temperate or at most hot temperate character. Evidently the glaciation in the Permo-Carboniferous period cannot have been the consequence of a few degrees' lowering of the general temperature, as in the Plistocene period.

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[1]) It has not been established beyond doubt that the tillite of Katanga is equivalent to the Dwyka tillite, possibly it is older. There is still less certainty about the age of the tillite found by KOERT in Togo, at 7° N. lat. That discovered by BALL and SHALER in the upper river basin of the Kongo, between 3° and 5° S. lat. is without doubt Triassic. Possibly some of the tillites found at very low latitude are the ground-moraines of local old glaciers. (Cf. E. HENNIG in: Geologische Rundschau, Band VI, p. 154, (Leipzig 1915)].

From the fact that everywhere the Glossopteris flora appears after the Permo-Carboniferous glaciation, while in Australia and South Africa the Carboniferous Lepidodendron flora preceded this glacial period, it was, indeed, inferred that the new flora arose under the influence of the cold, and being adapted to cold, replaced the thermophile Lepidodendron flora. But this view must be relinquished now that the Glossopteris flora has been found in South Africa also under, even in the Dwyka tillite, and immediately above this Permo-Carboniferous ground-moraine, just as immediately above the Orleans tillite of South America (Brazil), a mixed Glossopteris-Lepidodendron flora. A fact of the same significance is the mixture of the Glossopteris flora with the flora of the Siberian and North Russian Upper Permian testifying to heat, together with which flora large Theromorphous reptiles lived. Nor have traces of ice been found there anywhere. Besides the plants of the Glossopteris flora are partly huge trees, partly large-leaved herbs; with Gothan it may be assumed that this flora physiognomically certainly did not present any differences worth mentioning from the Permo-Carboniferous flora of the Northern Hemisphere. Hence the Glossopteris flora did evidently not arise under the influence of glacial cold; on the contrary, it required heat, like the Lepidodendron flora.

But while these latter lowland floras existed under high temperatures, the immense ice-masses which transported the material of the Permo-Carboniferous tillites, were accumulated in the mountains.

There have been found convincing proofs of some glacial periods older than the Permo-Carboniferous one. In South Africa the existence of a lower Devonian tillite at Griquatown at 29° S.lat., and of a Silurian or Cambrian (perhaps even Algonkian) tillite at Clanwilliam at 32° S.lat., and at Capetown at 34° S.lat., established by Rogers and others. According to Holtedahl the tillite discovered by Reusch at 70° N.lat. on the Varangerfjord, in the most northern part of Norway, is Lower Silurian and was probably supplied by a local glacier. The Arctic seas of the whole Silurian period were, however, undoubtedly hot. Upper Algonkian tillites have been found in China on the Jangtsekiang at 31° N.lat. by Bailey Willis, and in South Australia at Adelaide at 35° S.lat. by Howchin. The very extensive tillites in the Canadian province of Ontario between 46° and 50° N.lat. discovered by Coleman are dated in the Middle Algonkian period. Still perhaps somewhat doubtful is the Permo-Carboniferous glaciation discovered by Weidman in Oklahoma at about 34° $^1/_2$ N. lat. Also the Permo-Carboniferous tillite of Boston at $^1/_2$ 42′ N.lat., described by Sayles.

Of a more local character is probably the Triassic tillite discovered by Ball and Shaler in Central Africa, between 3° and 5° S.lat.

On the ground of all this evidence it may be assumed that during the Proterozoic and Palaeozoic eras, which judging from the lead-content of uranium minerals may be estimated at from three to four times the whole later geological time, at least now and then the conditions were present for extensive accumulation of ice in the mountains, which conditions were absent thereafter. In view of the space of time they occupy, these events constitute a very important side of our problem, which might make us inclined to consider the condition in that long space of time as "normal" and miothermal (less hot), just as the present and Plistocene condition, in contrast to the Mesozoic-Tertiary "abnormal" and pliothermal (hotter) interval, in which no extensive glacial traces were found. We might also think of such very long pliothermal times as the latter, occupying from a fourth to a third of the whole space of time, in the Proterozoic and Palerozoic eras, interglacial periods of the highest order, which have alternated with the glacial periods proper. Judging from the best documented of these latter, the Permo-Carboniferous glacial period, pliothermal conditions were, however, present also then even in the neighbourhood of the ice. The circumstances that have led to ice accumulation in the Permo-Carboniferous period must at all events had been entirely different from those in the Plistocene-period. This renders it impracticable to continue the line from those earliest climatic conditions to the present times.

But still many geologists see no essential difference between the Permo-Carboniferous and the Plistocene glaciation. Both events are considered to be caused by an extension of a niveous polar climate on to the rainy region of a temperate zone, in consequence of an only slight temporary lowering of the temperatures during a miothermal condition already existing over the whole Earth. WILHELM RAMSAY [1]) and others have rendered it plausible that miothermal times are periods of vigorous mountain formation, in which extensive parts of the Earth's crust are raised to a considerable height, which then cause the mean temperature on the Earth to fall through stronger loss of heat by radiation, lively vertical circulation in the atmosphere and increased condensation of water vapour. Such a miothermal period is the time in which we live. Anorogenetic periods, as the whole Mesozoic era, with lower and levelled continents and mountains, were, on the contrary, pliothermal times. Then glacial deposits were formed nowhere, not even at high latitude.

However the variations of the assumed conditions of heat on the Earth and those of its relief do not always run parallel. The climatic mechanism described by W. RAMSAY can, evidently, be suppressed by more powerful factors than an elevated or low relief of the Earth. In an "anorogenitic phase" the Lower Silurian tillite on the Varangerfjord was deposited, the Lower Devonian in South Africa, the Triassic in

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[1]) WILHELM RAMSAY, Orogenesis und Klima. Helsingfors 1910.

Central Africa. On the other hand the orogenetic Tertiary period was not miothermal, and it is inconceivable that millions of years of orogenesis were required for the development of the Plistocene miothermal effect. Besides, if there is a foundation of truth in the contraction theory, which is too much neglected at present, the relation between orogenesis and climate may possible be opposite to what RAMSAY and others suppose it to be, and the long Mesozoic anorogenetic phase may be the result of the universally ackowledged pliothermal condition of that time.

Apart from the "generally hotter or less hot conditions" on the Earth, we have apparently only to do with another localisation of the same climatic types as those existing at present. In fact the characteristics of these are absent in none of the geological formations considered here, — with the exception of glacial deposits in the Jurassic, the Cretaceous, and the greater part of the Tertiary periods. Besides the characteristics of a hot climate at high latitude and of accumulation of ice at comparatively low latitude, also those of the dry regions are found in the different formations; deposits of rock-salt, gypsum, desert sand, far from the places were they are found in recent times. They are all geographically distributed quite differently from the present distribution.

Was this distribution in every geological formation, not quite irregular, after all, and possibly analogous to the present distribution of the types of climate?

A priori it seems that the answer to this question can only be affirmative. In virtue of the spheroidal shape of the Earth the heat received from the Sun by any point of its surface must always have been function of the geographical latitude. Hence not even in the hottest geological period can a perfectly uniform climate have prevailed over the whole Earth. There must always have existed a system of climatic zones analogous to the present one with anomalies of a corresponding nature as in the present climatic system, which are to be attributed to the distribution of water and land, the height of the land, and the presence of meridional mountain-chains. In this the Sun, practically the only source of heat of the Earth's surface, is assumed to be invariable. To account for the constantly modified localisation of the climate types it is then natural to assume displacement of the equator and the poles during the whole geological past. Under for the rest equal telluric circumstances, as considered by RAMSAY, and taken in general, the climatic zones must have been distinguished from each other then in the same degree and the irregularities of the zonic system must have been comparatively as small as they are at present.

W. KÖPPEN and A. WEGENER [1]) see the climatic conditions of the geological past from this point of view, considering them in the light of WEGENER's hypothesis of the continental drift. On the maps of the world giving the different geological formations constructed by WEGENER, are indicated in the first place the two dry climatic zones, necessarily to be expected at about 30° then northern and southern latitude, from the deposits of rock-salt, gypsum, and desert sand, and between them the large circle of the equator is traced, along which the coal is situated of the equatorial rainy zone. Outside the dry regions are found the rainy regions of the temperate zone equally characterized by coal deposits. The ground-moraines of a niveous polar climate are often absent. A glacial period can certainly, in KÖPPEN and WEGENER's opinion, be suppressed by extensive transgressions in the polar region. It may, however, be stated, that for a continent as Antarctica with the earlier annexes the required extensive covering with water is always improbable. Besides they assume the polar climate to have been comparatively mild during the Mesozoic and Eocene time. This, like other "disturbances" in the climatic system of their maps is chiefly ascribed by them to the varying distribution of land and water, and the ocean- and air-currents dependent on them. They now see the situation of these climatic zones, which have been thus empirically determined, change from formation to formation. The poles have, therefore, shifted, though only within certain narrow limits, and the continents have drifted. Hence the history of the climate of a place is very nearly the history of its position with regard to the pole and the equator.

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[1]) W. KÖPPEN and A. WEGENER, Die Klimate der geologischen Vorzeit. Berlin 1924.

KÖPPEN and WEGENER consider that in this way they have shown systems of climatic zones, in main lines equal to the present system and with irregularities of the same nature, for all formations from the Carboniferous to the Plistocene. For the Quaternary period the shift of the poles accounts for the Ice Age, but they ascribe the alternation of glacial and interglacial periods to the secular variations of the eccentricity, the perihelium, and the obliqueness of the Earth's orbit, with which the solar radiation received by the Earth varies and in consequence the summer heat.

They consider the Sun itself as a source of heat constant throughout the whole geological past up to the present time. Already on account of an earlier greater "solar constant" their explanation of the varying distribution of the climatic types would call for a modification, in as much as disproportionately more heat than at present was transported from low to high latitudes with the then greater atmospheric circulation and sea currents. But when besides the greater energy of solar radiation had another spectrum maximum, the heat received by the Earth might have been distributed more uniformly or less uniformly over its surface than at present on account of the different behaviour of the atmosphere and the hydrosphere of our planet towards solar radiation of different wave length. Then also the difference of temperature between high and low might have been smaller or greater, and the "disturbances" might in general have been comparatively smaller or more important than at present. Moreover with very considerable apparent size of the Sun, the heat directly received at any place of the Earth will, according to BLANDET's hypothesis, have been less dependent on the geographical latitude.

Under certain states of evolution of the Sun, in which it possibly may have been in the geological past, the climatic zonic system may, therefore, have been less pronounced, and there may have been disturbances of more importance than at present. If the Sun's radiation itself has changed during the Earth's past, the history of the climate of a place is *not* chiefly the history of its situation with respect to the equator and the pole, plants and animals of a hot climate may have lived at comparatively short distance from a former pole and also from highlands covered with ice, and ice may have been accumulated at comparatively low latitude, isolated, and without polar connection.

Actually the following floras and faunas testifying to a hot climate existed at high latitudes on KÖPPEN and WEGENER's maps, also when there was ice at those places:

The prae-, inter-, and postglacial Permo-Carboniferous flora in South Africa at 70° to 80° S. lat., in Australia at 70° S. lat., in South America, in the Falkland-Islands, and in the Antarctic continent between 60° and 70° S. (Gangamopteris was also found *in* the Dwyka tillite).

The Permian large Theromorphous reptiles: Pareiasaurus, Dicynodon and others in South Africa at 55° to 60° S. lat. (Their nearest relations lived at 30° N. lat. in Northern Russia, like other Theromorpha: Dimetrodon, Naosaurus and others in Texas. The fresh-water reptile Mesosaurus, which is indeed only 70 cm. long, is found immediately on the Dwyka tillite).

The Triassic reef corals in California and Oregon near and beyond 60° N. lat. to Alaska at 75° N. lat.¹).

The Triassic large Theromorpha: Cynognathus and others in South Africa at 60° S.

The Lower Jurassic large Dinosauria in South Africa at 60° S. lat.

The Jurassic flora in West Antarctica at 68° S. lat.

The large Dinosauria of the Lower Cretaceous Tendaguru fauna in East Africa at 53° S. lat.²) and the closely allied Como fauna of the same time, and also the Upper Cretaceous large Dinosauria in North America at about 45° to 50° N. lat.

The Upper or Middle Cretaceous large Dinosauria in North Patagonia at 60° to 70° S. lat.

The Under Cretaceous flora of Uitenhage in South Africa at 67° S. lat. and the Upper Cretaceous flora in South Patagonia at about 65° S. lat.

The Eocene hot-temperate leaf-tree flora in Alaska at 60° to 70° N. lat.

The probably Tertiary hot-temperate Fagus flora of the region about

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¹) In KÖPPEN and WEGENER's text p. 63, Triassic coral reefs in Oregon erroneously at "fast 40°".

²) In KÖPPEN and WEGENER's text p. 92 "damals 35° S.," propably printer's error.

the Strait of Magellan at 60° to 70° S. lat. (if however Plistocene at only about 30° S. lat.) and the probably Tertiary subtropical flora in Seymour island at 70° to 75° S. lat. (if Plistocene yet higher than 50° S. lat.).

The Eocene nummulites in the northern part of Madagascar to 67° S. lat. on the west coast.

The Miocene and Lower Pliocene Anthropoid Apes in Europe: Dryopithecus and Pliohylobates to about 37° N. and Pliopithecus to about 38° N.

The Upper Miocene Santa-Cruz fauna in Patagonia with Homunculus and Nesodon and others at at least 50° S. lat.

The Pliocene (or Lower Plistocene?) marine warm-water fauna of Nome in Alaska at at least 67° N. lat.

The Upper Pliocene (= Lower Plistocene) flora and fauna of Tegelen at 57° N. lat. and the simultaneous fauna of Cromer at 59° N. lat.

The Upper Pliocene (= Lower Plistocene) Megalonyx fauna in North America to 65° N. lat.

This palaeontological evidence, which might easily be added to, may suffice to prove that the shift of the poles and the drift of continents alone are not sufficient to solve the palaeontological problem. KÖPPEN and WEGENER acknowledge this for the Mesozoic and Eocene periods, but it applies equally well to the Palaeozoic and the Neogene period.

At comparatively low latitudes of KÖPPEN and WEGENER's maps ice is actually found accumulated outside polar connection. The Triassic tillite discovered in Central Africa between 3° and 5° S. lat. lies, on their map, at 38° S. lat., i.e. at a greater distance from the Triassic pole and too much isolated to have arisen through polar cold climate. The same thing holds for the Boston- and Oklahoma tillites, which however perhaps somewhat dubious, lie at about 15° N. lat. and 22° N. lat. with regard to the Permo-Carboniferous north pole. Nor do the directions of movement of the Permo-Carboniferous ice-sheets in South Africa, which are independent of the hypothetical Permo-Carboniferous (and the present) south pole, testify to polar glaciation. If circumpolarly glacial, the Upper Algonkian tillites on the Jangtsekiang would require much greater displacement of the pole than KÖPPEN en WEGENER assume from the present to the Carboniferous period. From the Cretaceous to the Carboniferous period, this point always was under or close to the equator of their maps.

However meritorious in details, the hypothesis of the shift of the poles and the drift of the continents, therefore, leaves the palaeothermal problem at bottom for the greater part unsolved. As further all the other attempts at telluric explanations have proved inadequate, as far as the essential part of the problem is concerned, the solution apparently must be found in the changes indicated above, of the quantity and the quality of the energy radiated by the Sun, in its evolution, to our planet, during the geological time. The successive genesis of the geological formations and the development of the vegetable and the animal world on the Earth must then have kept pace with this evolution.

According to the giant and dwarf theory of stellar evolution drawn up by HENRY NORRIS RUSSELL in 1914, the principle of which had already been acknowledged by EJNAR HERTZSPRUNG in 1905, who also introduced the names of "giants" and "dwarfs",our Sun at first was in the state of a giant star of great dimensions but slight density, of rising temperature and with a maximum of the energy of radiation and colour shifting from red to yellow and further in the spectrum. After a certain maximum of temperature and certain smallest wave-length of maximum energy of radiation in the spectrum had been reached, the Sun entered the phase of a shrunken but dense dwarf star.of descending temperature. The maximum of the energy of radiation in the spectrum and the colour now shifted in the opposite direction, towards the red, so that our yellow dwarf sun has passed its present temperature and spectral stage already once, viz. as a giant star. In the giant stage the dimensions gradually diminished, but at the same time the temperature rose so that the total intensity of radiation remained the same throughout this whole phase. In the dwarf stage, on the other hand, the Sun became smaller with descending temperature, so that the total intensity of radiation steadily diminished.

The highest temperature reached in the giant phase and the smallest wave-length of the maximum of radiation in the spectrum reached corresponding to it, depends on the mass of the star. The maximum temperature is comparetively low in a scarcely middle-sized star like the Sun, and the displacement of the maximum energy of radiation in the spectrum from the red, has been comparatively small. At present the Sun is in the condition of a yellow dwarf star, in the middle of the *G*-class of the Harvard-classification, and its effective temperature is about 5900° abs. The temperature maximum at the transition from the giant- to the dwarf phase was calculated at 6600° abs. by EDDINGTON (1922). It may have been still less high. At such a maximum temperature the Sun as giant star has probably never reached the stage of the *F*-class. With the Harvard classes *A* and *B* following in the ascending series of the temperatures, this belongs already to the First class, of the "White Stars", according to the earlier classification of SECCHI. During its giant phase the Sun first belonged to the *M*-class, corresponding to the Third class, of the "Red Stars" of SECCHI, then to the reddish yellow *K*-stars, which with the *G*-stars constitute the Second class, of the "Yellow Stars" in the earlier classification, and to all the transitions between the *M*- and the *K*-stage and between the *K*- and the *G*-stage, till the highest point of the giant phase above the *G*-stage was reached. According to WIEN's law a displacement of the maximum of energy in the spectrum to a wave-length about 0.9 times the value from about 570 $\mu\mu$ in the yellow to 510 $\mu\mu$ in the green corresponds to a change of temperature from 5900° ot 6600° , and according to STEFAN's radiation law a total intensity of radiation almost one and a half times the value ¹). But these are probably extremes. If the maximum of the temperature in the Sun's evolution curve lay close above the *G*-points, the total intensity of radiation in the giant phase was not much greater than in the present condition of the Sun, and the spectral radiation has changed only little since the highest temperature had been reached.

The views about the sources of the stellar energy of radiation and the cause of the change of the giant phase into the dwarf phase, hence about the internal nature of stellar evolution, have undergone important modifications and extension since the new theory was drawn up, especially of late years, through the work of EDDINGTON, JEANS and others, and chiefly in connection with the results of modern physics. These views themselves are still in a state of evolution, but to all probability the conception of the course of stellar evolution, which we owe to HERTZSPRUNG and RUSSELL, will remain unaffected.

For the Sun's evolution ages are calculated hundreds of times greater than the geological past considered here. It seems, therefore, to be entirely inadmissible to connect this evolution with the palaeothermal events discussed in this communication. But in the calculations of the Sun's age there is still so much uncertainty, chiefly on account of insufficient knowledge of the internal nature of stellar evolution, that the possibility at least remains that the whole or a large part of the giant phase of the Sun and the part of its dwarf phase passed through up to now, coincide with the geological time ²). This possibility becomes probability when we consider the palaeothermal problem in the light of the giant and dwarf theory.

If it is an established fact that the Sun was still a giant star comparatively shortly ago, it must have passed the greater part of its past as a reddish yellow giant star of the *M*- and *K*-classes. The total radiation was then greater, just as in the whole giant stage, but not very much greater than the present radiation, but the maximum of energy lay in or near the red, and on the whole the radiation was of greater wavelength than at present. Besides the volume was really gigantic, especially in the *M*-stage, and the apparent size very considerable.

The long time of the Sun's past as much less hot red or reddish giant star, or at least a large part of it, may be considered in connection

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¹) According to the same law about 35° C. (against 3° C. now) is found for the Earth's mean effective temperature under the hottest sun, ceteris paribus. The calculated temperature at the surface of the Earth would have been still higher. The real temperatures must have remained far below this on account of the much greater albedo.

²) Cf. the end of J. H. JEANS's article: On the Masses, Luminosities, and Surface-Temperatures of the Stars. Monthly Notices R. Astron. Soc. Vol. 85, January 1925, p. 211.

with the long Protero- and Palaeozoic time, in which "Ice Ages" occurred more than once. Then the Earth received, indeed, more solar radiation than at present, but of lower temperature, and also of another quality as regards its relation to the atmosphere and the hydrosphere. It should be remembered that the atmosphere acts in two ways on the solar radiation that passed through it. First through its water-vapour and carbonic acid it absorbs all the solar radiation and also the dark radiation emitted again by the heated Earth at certain places in the red part of the spectrum and far beyond it : *selective absorption*. Secondly it absorbs more or less of the energy of the whole radiation, on account of internal reflections at the air-molecules and other small particles which scatter them in all directions. This makes the atmosphere itself source of light and heat, the great significance of which has only been realised quite recently. The "diffuse daylight" and "the blue shy light is at the same time radiation of heat. Lord RAYLEIGH has shown that *this diffuse reflection* is in inverse ratio to the fourth power of the wave-length; hence it is slight for red and yellow, great for blue and violet rays. Also in water the short-wave rays undergo strong dispersion, and return to the atmosphere for the greater part, the red and ultra-red rays, on the other hand, are absorbed. Thus the energy of radiation of short wave-length is chiefly communicated to the high atmospheric layers, those of great wave-length, on the contrary, to the lower atmospheric layers, which are rich in water-vapour and carbonic acid, and to the hydrosphere.

It is, therefore, easy to see that where in the Protero- and Palaeozoic eras there were extensive highlands even at comparatively low latitudes, as there certainly were at the end of the latter period in the Southern Hemisphere, large ice-masses must have accumulated on the strongly radiating highlands in the badly heated upper air, more isolated also on mountains of the lowest latitude; we see the latter even as late as the Triassic period. The lowlands and the sea being well heated, there was strong vertical circulation in the atmosphere, consequently sufficient supply of water-vapour towards the highlands for accumulation of snow-ice. For the rest the niveous circuit is many thousands of times slower than the pluvial circuit, and large ice-sheets can already be formed with slight snowfall during thousands of years (examples of this are Antarctica and Greenland). In the lowlands and in the sea, which were hot to the highest latitudes on account of the strong currents, caused by the high "solar constant" and the strong absorption of the red radiation, hot-climate plants and animals could live, even near the ice-covered highlands. Possibly the considerable apparent size of the then giant sun also contributed to making the climate hot at high latitude.

As the different conditions of the Sun's development gradually passed into each other, just as the geological formations do, this long first period cannot be sharply defined in either way. Probably it was much longer than the whole period succeeding it, for the temperature rose to double its value in the giant phase from the *M*-stage to the *G*-stage, and after it to the highest point of the giant phase only still about a tenth. In this respect the Mesozoic period may probably be brought in connection with the *G*-giant stage to the maximum of the Sun's evolution. With an intensity of radiation or "solar constant" of the same value the distribution of energy over the spectrum was the same in the *G*-stage as at present. Further with maximum of energy shifted still more away from the red, the wave-lengths of the spectrum were on the whole at the highest temperature smaller than ever before or after. In this period the rays of short wave-lengths obtained more and more importance compared with the long-wave ones, ultimately even more than they have in the present condition of the Sun. The upper atmospheric layers were more heated at the time than before, and air masses charged with great quantities of entropy in equatorial regions and capable of radiation were now carried to high latitudes by the general circulation of the atmosphere operating especially powerfully in winter; they thus contributed greatly to the more uniform distribution of the heat over the earth, in the way as has been shown for the present time especially by EMBDEN. This mechanism must have been more powerful than at present on account of the greater "solar constant", in consequence of which a much more uniform climate must have prevailed over the whole Earth, at the same time the differences of temperature between high and low were much smaller than before, and in general the highlands could not become sufficiently cold for accumulation of ice.

But in the dwarf phase the temperature fell and the maximum of energy in the spectrum was displaced in the direction towards the greater wave-lengths. At the same time the total intensity of radiation, the "solar constant", decreased, and ultimately the present condition of a dwarf star which is in the middle of its *G*-stage, was reached. At this maximum of the giant phase a new epoch in the Sun's life does, therefore, really start. The effect of the low temperature on the intensity of radiation has no longer been cancelled since then by certain (insufficiently known) factors, which kept the intensity of radiation equal in the giant phase, and this while the heating of the upper atmospheric layers and the diminution of the want of uniformity in the distribution of the heat over the Earth caused by it, decreases. If this dwarf period is assumed to run parallel with the Neozoic period, it becomes comprehensible that climatic zones began to take definite form, and that at last the whole Earth got into a really miothermal condition with real general glacial periods.

When this view is held, great revolutions in the biosphere, the causes of which remain else perfectly unaccountable, are still more easily accounted for than in the light of the earlier views about the evolution of the Sun. Already shortly after the beginning of the Cretaceous period, i.e., according to the synchronism assumed, still before the turning-point in this evolution, the new epoch of the vegetable world sets in, in which the Angiospermal leaf trees predominate, which in contrast to the Mesozoic Gymnospermal flora, which was then for the greater part dying out, possess a very great total leaf-surface. This great revolution in the vegetable world may now be considered as an adaptation to the quantity of red radiation, which was then becoming minimum. For it is this radiation, to which the principal absorption band of the chlorophyl corresponds, that chiefly brings about the carbonic acid assimilation at the slight light intensity under which the leaf operates according to WIESNER's researches. It is also available already in the early morning and still late in the evening. The chlorophyl of this time is evidently the same green colouring matter as in the oldest carbonic-acid assimilating plants.

The greatest revolution in the animal world occurs somewhat later. The largest forms of the class of Reptiles, a number of orders, die out at the end of the Mesozoic era. This is accompanied at the beginning of the Neozoic era by the rapid and rich development of the class of Mammals, which was only represented by a few small, scarcely changing forms from the Triassic period to the end of the Cretaceous period. In fact the predominance in the animal world passes from the Reptiles to the Mammals. The Neozoic period is the Age of Mammals, as the Mesozoic period was the Age of Reptiles. It is natural to seek a connection between this revolution and the general diminution of heat in the high latitudes starting at the turning-point of the Sun's evolution. Large Reptiles, being animals entirely dependent on the heat of their surroundings, could no longer in general exist then at high latitude. Mammals, on the other hand are in a high degree independent of the temperature of their surroundings on account of their own heat. This class could, therefore, not but occupy the places in the biosphere left vacant by the extinct Reptiles, as we actually see in many convergent developments.

The new stellar evolution-theory thus throws a clear light on some of the most important problems met with in the investigation of the Earth's crust.

May the discussed, well established geological facts contribute to the further development of this theory!

Microbiology. — *"The catalytic transference of hydrogen as the basis of the chemistry of dissimilation processes."* By A. J. KLUYVER and H. J. L. DONKER. (Communicated by Prof. G. VAN ITERSON Jr.).

(Communicated at the meeting of February 28, 1925).

§ 1. *Introduction.*

As far back as 1876 PASTEUR[1]) expressed the opinion, that the fermentation processes of anaerobic organisms must be considered as a substitute for the respiratory process of aerobic organisms. Later researches have convincingly proved the correctness of this view. It appeared from these researches that the significance of both fermentation and respiration lies in the fulfilment of the energetic requirements of the living cell, for which reason both processes can be collected under the general term: dissimilation processes. In addition it was shown, that the similarity in physiological function expressed itself also in the chemical reactions brought about. Numerous investigations have made it in a high degree probable, that when sugar functions as substrate of respiration, with aerobic organisms, both animal and vegetable, as a rule the free oxygen intervenes only after the sugar has undergone an anaerobic transformation.[2])

Although the discovery of the anaerobic phase in the respiration process has removed the contrast between the processes of oxidative and fermentative dissimilation of sugar to a remarkable extent, still this does not take away the gulf still existing between these two ways of providing energy, as long as the final phases apparently differ so much.

Here and there in more recent literature some remarks are already to be found which also point to the similarity of certain partial changes in the *aerobic* phase of respiration and some reactions occurring in fermentation. It is the aim of this communication to demonstrate that in reality the same chemical process lies at the basis of both aerobic and anaerobic respiration processes.

§ 2. *The chemistry of the oxidation processes in aerobic respiration.*

With a view to subsequent considerations it is desirable first of all to study more closely the chemistry of the oxidation processes occurring in aerobic respiration. As is well known, these are oxidations which do not proceed of their own accord at ordinary temperatures and which take place in the organism under the catalytic influence of the living protoplasm of the cells. It is obvious that biologists have tried to get a better insight into the mechanism of this catalysis. A number of investigators are of the opinion that the action of the living cell consists before all of an activation of the oxygen necessary for combustion. Opposed to this, a theory has been put forward by H. WIELAND, according to which the catalytic action of the protoplasm will depend on an activation — eventually after a preliminary hydration — of hydrogen atoms present in the substrate, which atoms in this active state are then able to combine with the oxygen. ^{1})

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[1]) L. PASTEUR, Etudes sur la bière, Paris 1876, pag. 229 et seq.

[2]) Reference may be made in this connection to: O. MEYERHOF, Ueber den Zusammenhang von Atmung und Gärung, Die Naturwissenschaften vol. 7, p. 253, (1919); also: O. MEYERHOF, Chemical Dynamics of Life Phaenomena, Philadelphia, 1924, Chapter III and to: S. KOSTYTSCHEW, Pflanzenatmung, Berlin, 1924.

WIELAND finds strong support for this opinion in his researches on the catalytic oxidation of organic compounds under the influence of inorganic catalysts such as palladium black. With the aid of this catalyst WIELAND was able to oxidise alcohol to acetaldehyde and the latter in the presence of moisture to acetic acid. That we have to do here firstly with a hydrogen removing action of the catalyst, is made very acceptable, because the oxygen used for the oxidation can be quite succesfully replaced by other so-called hydrogen acceptors such as methylene blue or quinone. Besides this the hydrogen activating action of the catalyst is especially evident from the fact that in the absence of any hydrogen acceptor the splitting off of hydrogen can be established without doubt. By showing that acetic acid bacteria are able to oxidise alcohol to acetic acid by making use of methylene blue instead of oxygen, WIELAND extended his dehydrogenation theory to the chemistry of biological oxidations.

In the meantime O. WARBURG has advanced quite another theory on the chemistry of the oxidation processes in aerobic respiration based upon an extensive series of extremely important experiments. ^{2}) In these investigations WARBURG showed that traces of iron present in an unknown organic combination are able to transfer catalytically free oxygen to a number of substances, amongst which several biochemical oxidation substrates are to be found. It is easily to be understood that WARBURG wants also to ascribe the catalytic action in the respiratory process to iron, which element is always present in the living cell. A further proof of the correctness of this view is seen by WARBURG in the fact that hydrocyanic acid inactivates the oxidative action both of the „carbon

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^{1}) See: H. WIELAND, Ergebnisse der Physiologie, vol. 20, pag. 477, (1922); idem Ber. vol. 55, p. 639, (1922) and also WIELAND's Synopsis in OPPENHEIMER's „Handbuch der Biochemie" 2nd Ed., Jena, 1923. vol. II. p. 252.

^{2}) Compare: O. WARBURG, Biochem. Zeitschr. vol. 119, p. 134, (1921); ibid. vol. 136, p. 266, (1923); ibid. vol. 142, p. 518, (1924); ibid. vol. 145, p. 461, (1924); ibid. vol. 152. pag. 479, (1924).

model" and of the living cell in stoechiometric relation to the iron present.

WARBURG criticizes WIELAND's theory of hydrogen activation very strongly, as may appear from his statement: „Da es keinen Versuch gibt, der die Theorie begründet und keine Consequenz der Theorie die zutrifft, so soll sie in der Folge nicht mehr berücksichtigt werden."

Lack of space forbids us here to enter into the polemics carried on in various places by WARBURG and WIELAND. We will content ourselves by giving as our opinion that both theories in their present mode of representation are untenable, yet on the other hand both contain elements with the help of which the observed phenomena can be explained in a completely satisfactory way. ¹) The experiments of WARBURG make it most highly probable that in biological oxidations molecular oxygen is intermediately attached to an organic iron compound by which means the oxygen is converted into an active state. ²) However, the opinion of WARBURG, that oxygen taken up by the iron compound should be able to oxidise the oxidation substrate straight away and that the catalytically acting iron compounds should be the only agents acting in respiration, is not in agreement with the facts.

Against this, among many arguments, is the replaceability of molecular oxygen by reducible substances like methylene blue or quinone, in which case the living cell is likewise indispensable as a catalyst and the catalysis is possible without the cooperation of an iron compound, since the process is insensible to cyanides. Further the selective action of the living cell towards different oxidation substrates cannot be easily brought in agreement with WARBURG's theory.

On the other hand, if we assume with WIELAND that the action of living protoplasm as a catalyst in the respiratory process consists of a dehydrogenation of the respiration substrate and a transference of the activated hydrogen to a hydrogen acceptor, then the observed phenomena find an easy explanation, if we also introduce the secondary hypothesis, that in opposition with other acceptors, free oxygen can only act as a hydrogen acceptor after combination with iron.

The theory of the hydrogen activating action of protoplasm finds its strongest support in the fact, that — as will be seen below — it puts us in a position to obtain an insight into the chemistry of anaerobic dissimilation processes, by which the apparently essential difference in the chemistry of aerobic and anaerobic dissimilation processes is reduced to a gradual one.

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¹) After this communication was in the press, it came to our notice that this opinion was expressed earlier and made probable on experimental grounds by A. v. SCENT-GYÖRGYI. See: Biochem. Zeitschr. vol. 150, p. 195, (1924). *[Note added during correction]*.

²) The earlier well-known researches of ENGLER and WEISZBERG on the autoxidation of various organic substances, in which it was shown conclusively that molecular oxygen reacts in the first instance only with the formation of moloxides, supports this view.

§ 3. *The chemistry of fermentative dissimilation processes.*

As we have set forth in a previous communication¹), it appears that on closer examination the fermentative sugar dissimilation processes of microbes may be reduced to a number of coupled dehydrogenation and hydrogenation reactions along with intramolecular changes and condensation reactions.

We will now fix our attention on the first mentioned type of reaction which can be brought back to a catalytic transference of hydrogen.

In the paper mentioned above we were satisfied in giving a representation as if the dehydrogenation simply existed in the formation of a compound of protoplasm and hydrogen from which the protoplasm was regenerated either spontaneously or by the transference of the hydrogen to other compounds (hydrogenation). Meanwhile this conception is too simple and it is necessary to consider this catalytic process more particularly.

We may suppose, that during the first part of the catalysis: the dehydrogenation, the protoplasm exerts an influence on the substrate, leading to an alteration in the latter substance, which is termed by BÖESEKEN in his discussions on catalysis²) as "dislocation".

The consequence of this alteration is, that one or more hydrogen atoms present in the substrate become less firmly bound, or in other words: become activated.

This dislocation is undoubtedly a result of the chemical affinity of the catalyst for the dehydrogenation substrate or more precisely for the atoms present in this substrate.³) Since a portion of the affinities of these atoms is saturated by the affinities of the catalyst the bonds between the atoms in the molecule are weakened.

We now have to consider how this dislocation leads in certain cases to an activation of hydrogen. Therefore it should be pointed out, that undoubtedly the affinity of the protoplasm for the dehydrogenation substrate may be brought back more especially to the affinity of the protoplasm for the hydrogen and oxygen atoms of the substrate. It must be understood that the affinities for hydrogen and oxygen are not independent properties, but that these properties are so connected that a large affinity for oxygen always means a small affinity for hydrogen and vice versa, as is also shown in the behaviour of metals towards these elements.

That an affinity of the protoplasm for hydrogen can give rise to an activation of the hydrogen atoms present in the substrate can be illustrated as follows. The saturation of a part of the affinity of the hydrogen by that of the catalyst, which in itself is unsaturated, will have in con-

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¹) These Proceedings vol. 28, p. 297, (1925).

²) Compare e. g.: J. BÖESEKEN, These Proceedings, vol, 25, p. 210, (1922).

³) Compare also: H. J. PRINS, Bijdrage tot de kennis der katalyse, Proefschrift Delft 1912 and „Over het verband tusschen katalyse en affiniteit", Chemisch Weekblad, vol. 14, p. 63, (1917).

sequence, that the hydrogen remains bound to the substrate rest with a smaller affinity and so this rest will be brought to a state of unsaturation. Meanwhile this condition has the immediate result that the affinity set free tries to neutralize itself somewhere else in the molecule. As this tendency is more or less fully satisfied, or in other words in proportion as more definite translation of atoms in the molecule occurs, the hydrogen will remain bound with a smaller affinity to the rest of the molecule, which means activation. In the extreme case this will lead to the transformation of the remainder of the molecule into a completely saturated compound whereby the hydrogen will be completely liberated by this remainder. In this connection it is to be borne in mind that the amount of hydrogen activation is at the same time dependent on the affinity with which the protoplasm combines with the hydrogen. If this last mentioned affinity is too small only a small activation of hydrogen will occur because the hydrogen remains too firmly attached to the rest of the molecule; if the affinity in question is too big, there is neither an optimum activation, because the hydrogen is now fixed firmly, it is true no longer to the rest of the molecule, but to the protoplasm. In this case, as PRINS remarks, the catalyst as a catalyst exceeds its aim.

Hence it is obvious that the optimum hydrogen activation in different substrates will be smaller in proportion as the hydrogen, which is activated, was bound more firmly in the substrate, while, to obtain the optimum activation a greater affinity of protoplasm for hydrogen is necessary. On the other hand this brings along with it, that a protoplasm with relatively small affinity for hydrogen will be able to activate hydrogen only from dehydrogenation substrates with relatively weakly bound hydrogen, and yet in that case the resulting activation will be much larger than in the case of hydrogen activation from such a substrate under the influence of a protoplasm with a greater affinity for hydrogen.

Meanwhile not only can the activation of hydrogen be the result of a predominent affinity of protoplasm for hydrogen, but the affinity of protoplasm for oxygen may similarly give rise to hydrogen activation. This can be illustrated as follows. Let us consider firstly those dehydrogenation substrates in which the activated hydrogen is in a hydroxyl group. In this case, on the grounds of similar considerations as set forth above, it will be seen that saturation of a portion of the affinity of the oxygen of the hydroxyl group by that of the unsaturated catalyst, will have the consequence, that the oxygen is combined with hydrogen with a smaller affinity, or in other words, the hydrogen will be activated. If now the extreme case occurs, where the remainder of the molecule completely releases the hydrogen atom, these atoms of hydrogen are set free and combine to gaseous hydrogen, in contrary to what is the case if the activation is caused by the affinity of protoplasm for hydrogen.

Now it still remains for us to explain how the affinity of the protoplasm for oxygen can lead to the result that in oxygen containing dehydrogenation substrates other hydrogen atoms than those, which are situated in hydroxyl groups, are activated. As the protoplasm grasps a part of the affinity of the oxygen there will be a weakening of the bond between the oxygen and the remainder of the molecule, and so the atom of this remainder to which the oxygen is bound will become unsaturated and will try to compensate the loss by taking up affinity from some other part of the molecule. In consequence of this there can be activation of hydrogen somewhere else in the molecule [1]).

It will be clear that, at any rate in oxygen containing dehydrogenation substrates, the activation of hydrogen will always be the result of both the affinity of the protoplasm for hydrogen and that for oxygen. Both influences will act supplementary; yet since a large affinity for hydrogen always brings along with it a small affinity for oxygen and vice versa, as a rule one will have to do only with one of these factors [2]).

Considering now the second part of the process of the catalytic transference of hydrogen, evidently only these substances lend themselves to act as hydrogen acceptors which are more or less easily reducible. It will be quite clear that the protoplasm will also take up (partially) affinities of the hydrogen or oxygen atoms of the molecule acting as a hydrogen acceptor. As a sequence, centres of unsaturation will be produced in the part of the molecule which binds these atoms, leading to an activation of the acceptor, which increases the tendency for hydrogenation.

If, and with what velocity, a particular hydrogen transference will take place, is exclusively dependent on the reduction tendency of the activated hydrogen acceptor, and on the degree of hydrogen activation in the dehydrogenation substrate, which activation — as we saw above — is in its turn a function of the strength of the bond between the hydrogen to be activated and the dehydrogenation substrate, and of the degree of affinity of the protoplasm for hydrogen and oxygen respectively.

Let us now direct attention to the intramolecular changes and condensation reactions mentioned at the beginning of this paragraph. A closer examination shows that also these parts of the chemistry of fermentative dissimilation processes are in reality nothing but changes in which hydrogen is catalytically transferred. To elucidate this view we may refer in the first place to the following scheme.

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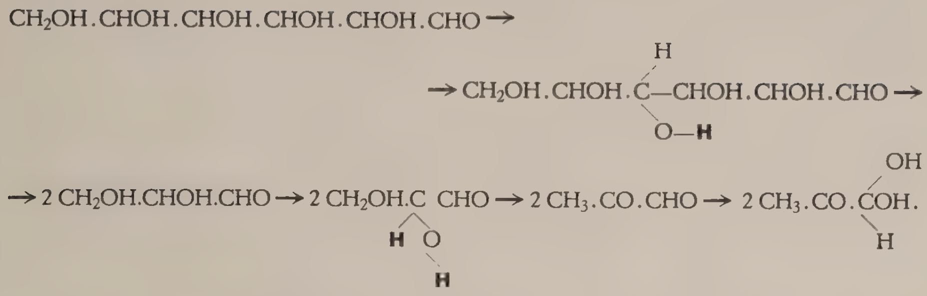
[1]) This idea is in agreement with thc views of H. J. PRINS, who describes in his study „The Mechanism of Reduction" Rec. trav. chim. vol. 42, p. 473, (1923), how the affinity of a catalyst for oxygen can lead to the activation of hydrogen. Compare also § 4 p. 617 of this communication.

[2]) An analogy of this situation is found in the hydrolysis of esters which is accelerated by both hydrogen ions and hydroxyl ions. In an acid medium only the action of the former ions, in an alkaline medium only that of the latter ions, is of practical importance.

SCHEME [1]

I. *Initial change.*

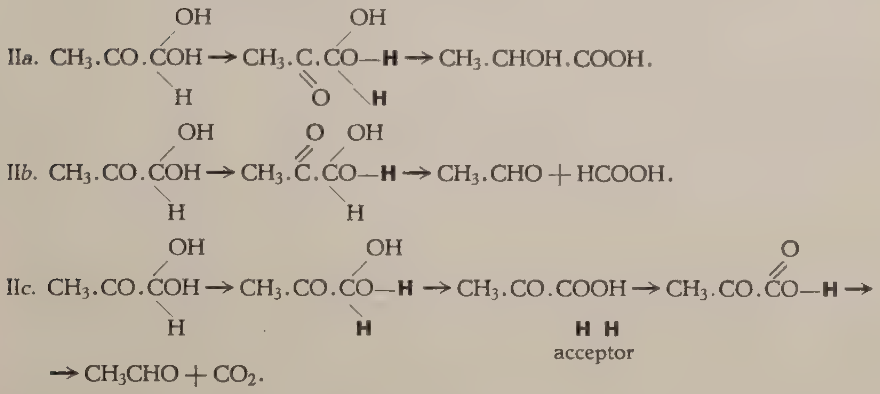


$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO \rightarrow$$

$$\rightarrow CH_2OH.CHOH.\overset{H}{\underset{O-\mathbf{H}}{C}}-CHOH.CHOH.CHO \rightarrow$$

$$\rightarrow 2\,CH_2OH.CHOH.CHO \rightarrow 2\,CH_2OH.\underset{\mathbf{H}\;\underset{\mathbf{H}}{O}}{C}\;CHO \rightarrow 2\,CH_3.CO.CHO \rightarrow 2\,CH_3.CO.\overset{OH}{\underset{H}{C}}OH.$$

II. *Conversions of the hypothetic intermediate product.*



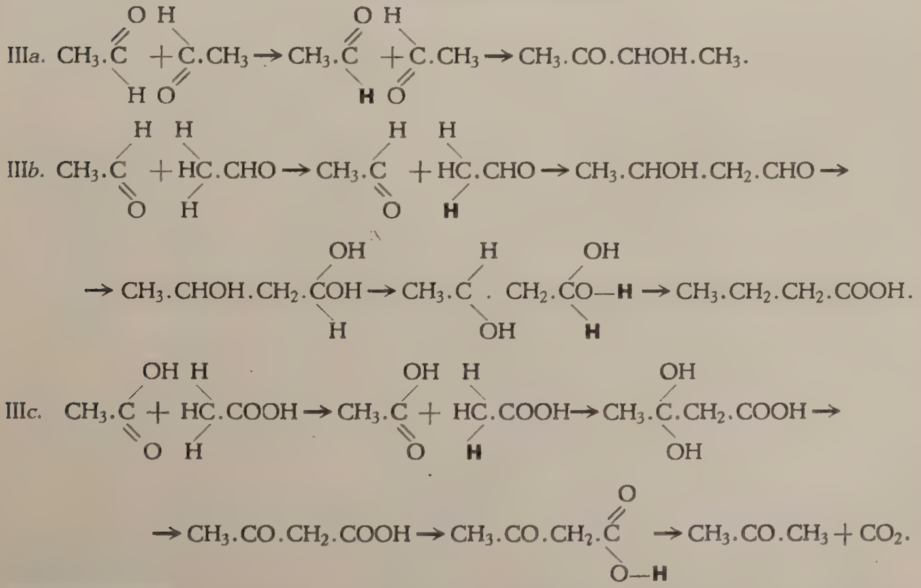
$$\text{IIa.}\;CH_3.CO.\overset{OH}{\underset{H}{C}}OH \rightarrow CH_3.\underset{O}{C}.\overset{OH}{\underset{\mathbf{H}}{C}}O-\mathbf{H} \rightarrow CH_3.CHOH.COOH.$$

$$\text{IIb.}\;CH_3.CO.\overset{OH}{\underset{H}{C}}OH \rightarrow CH_3.\overset{O}{C}.\overset{OH}{\underset{H}{C}}O-\mathbf{H} \rightarrow CH_3.CHO + HCOOH.$$

$$\text{IIc.}\;CH_3.CO.\overset{OH}{\underset{H}{C}}OH \rightarrow CH_3.CO.\overset{OH}{\underset{\mathbf{H}}{C}}O-\mathbf{H} \rightarrow CH_3.CO.COOH \underset{\substack{\mathbf{H}\;\mathbf{H}\\ \text{acceptor}}}{\rightarrow} CH_3.CO.\overset{O}{C}O-\mathbf{H} \rightarrow$$

$$\rightarrow CH_3CHO + CO_2.$$

III. *Condensationreactions.*



$$\text{IIIa.}\;CH_3.\overset{O}{\underset{H}{C}} + \overset{H}{\underset{O}{C}}.CH_3 \rightarrow CH_3.\overset{O}{\underset{\mathbf{H}}{C}} + \overset{H}{\underset{O}{C}}.CH_3 \rightarrow CH_3.CO.CHOH.CH_3.$$

$$\text{IIIb.}\;CH_3.\overset{H}{\underset{O}{C}} + \overset{H}{\underset{H}{HC}}.CHO \rightarrow CH_3.\overset{H}{\underset{O}{C}} + \overset{H}{\underset{\mathbf{H}}{HC}}.CHO \rightarrow CH_3.CHOH.CH_2.CHO \rightarrow$$

$$\rightarrow CH_3.CHOH.CH_2.\overset{OH}{\underset{H}{C}}OH \rightarrow CH_3.\overset{H}{\underset{OH}{C}}\;.\;CH_2.\overset{OH}{\underset{\mathbf{H}}{C}}O-\mathbf{H} \rightarrow CH_3.CH_2.CH_2.COOH.$$

$$\text{IIIc.}\;CH_3.\overset{OH}{\underset{O}{C}} + \overset{H}{\underset{H}{HC}}.COOH \rightarrow CH_3.\overset{OH}{\underset{O}{C}} + \overset{H}{\underset{\mathbf{H}}{HC}}.COOH \rightarrow CH_3.\overset{OH}{\underset{OH}{C}}.CH_2.COOH \rightarrow$$

$$\rightarrow CH_3.CO.CH_2.COOH \rightarrow CH_3.CO.CH_2.\overset{O}{\underset{O-\mathbf{H}}{C}} \rightarrow CH_3.CO.CH_3 + CO_2.$$

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[1] This scheme gives the reactions taken under the same headings in Table II of our paper cited previously. Only it must be pointed out, that the reaction given under IIc has been newly added, which has to do with note 4 p. 306 of the previous paper,

An **H** printed in heavy type denotes an activated hydrogen atom.

As follows directly from this the particular intramolecular transformations are to be explained by assuming that the protoplasm exerts an activating influence on hydrogen atoms in the reacting substances. This dislocation of the molecule brings in its train a displacement of the affinities in the remaining part of the molecule, leading to the formation of a centre of unsaturation elsewhere in this molecule.

This centre will have the inclination to attract the activated hydrogen to itself or in other words to act as a hydrogen acceptor. In most cases when the hydrogen is transferred in this way, it leads to a rupture of the molecule and in others only to the transmigration of hydrogen and to consequent further changes of affinity within the molecule.

The peculiarity of this type of coupled dehydrogenation and hydrogenation is found in the fact that it is in a much less degree sensitive to an alteration in the affinity of the protoplasm for hydrogen or oxygen respectively. While in intermolecular transference of hydrogen a greater affinity of the protoplasm than the optimum has an adverse effect on the catalysis, as set out above, this is the case to a much smaller extent in intramolecular transference of hydrogen, because a protoplasm with greater affinity certainly fixes hydrogen to itself more firmly, yet on the other hand this stronger combination also brings along with it a more intensive unsaturation of the remainder of the molecule, which in this particular type of reactions itself acts as hydrogen acceptor, or in other words: simultaneous powerful activation of the acceptor takes place.

Finally it appears from the scheme given that also the condensation reactions can be reduced to the catalytic transference of hydrogen. Here the activated hydrogen is accepted by a second molecule of the same substance, which always contains an unsaturated group, while the affinities set free in such a molecule lead to the production of a new C—C bond.

Though we have limited ourselves here to a consideration of the fermentative sugar dissimilation processes of microbes, we will now indicate that the catalytic transference of hydrogen apparently also is at the basis of the chemistry of the fermentative sugar dissimilation processes of higher organisms. Also it is found again in dissimilation processes in which substances other than sugars form the substrate.¹)

§ 4. *The aerobic and anaerobic dissimilation processes as a function of the affinity of the living protoplasm for hydrogen.*

While it appears from the previous paragraph that the catalytic trans-

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¹) In this connection it may be pointed out in particular, that the process of fermentative dissimilation of amino acids by bacteria of the *Proteus*-group elucidated by NAWIASKY readily fits into the framework of the catalytic transference of hydrogen. See: Archiv für Hygiene, vol. 66, p. 209, (1908).

ference of hydrogen forms the nucleus of all fermentative dissimilation processes, we saw in § 2, that the oxidation processes which form the characteristic element of aerobic respiration, can also be made understandable with the assumption of such a transference. Considering the incontestable fact of the activation of hydrogen in a number of anaerobic dissimilation processes (evolution of gaseous hydrogen), the corresponding explanation of aerobic dissimilation processes finds its most powerful support in the unmistakable gradual passage of aerobic and anaerobic modes of life in each other. We will only refer here to the extremely numerous micro-organisms which in the absence of free oxygen provide for their energy requirements by a fermentation process, yet which in the presence of free oxygen derive the necessary energy from oxidative processes, which proceed with the absorption of oxygen.

We then come to the conclusion that the whole of the dissimilation processes of aerobic as well as anaerobic organisms in all their diversity may be brought back to the catalytic transference of hydrogen under the influence of the protoplasm present in these organisms [1]). In this way then the observed diversity in dissimilation reactions is only a consequence, following logically from the laws of chemical catalysis, of the gradual variation in affinity of the different kinds of protoplasm for hydrogen.

We shall elucidate this view further below, where we limit ourselves however to a very short discussion of those dissimilation processes in which a hexose occurs as a substrate.

I. Aerobic organisms with strong oxidative powers.

Examples: several kinds of moulds and acetic acid bacteria. The protoplasm of these organisms is characterised by a very great affinity for hydrogen. When oxygen is present as a hydrogen acceptor, glucose undergoes a direct dehydrogenation and gluconic acid is formed. Under optimum conditions gluconic acid as a rule is not found as a metabolism product but following on this change there takes place a whole series of further dehydrogenations and finally water and carbonic acid are produced.

Besides oxygen only such other powerful hydrogen acceptors as methylene blue (WIELAND) appear to be effective.

II. Aerobic organisms with weaker oxidative powers.

Examples: higher plants, (muscular tissue of the) higher animals, many aerobic spore forming bacteria. The hydrogen affinity here is so much smaller that the direct dehydrogenation of glucose with oxygen as hydrogen acceptor is not possible, yet instead of this intra-molecular dehydrogenation and hydrogenation occurs, which causes the sugar to break down into compounds of the C_3-type. In the presence of sufficient oxygen the methylglyoxal formed will be dehydrogenated. Under anaerobic conditions the methylglyoxal is converted by muscular tissue of higher animals into lactic acid by an intramolecular change. The lactic acid can undergo further dehydrogenation if oxygen is re-introduced [1]).

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[1]) In this connection it is well to remember a statement of T. THUNBERG (see for example: Die Naturwissenschaften, vol. 10, p. 417, 1922), who concluded after a closer discussion of aerobic respiration processes that „der Wasserstoff als das elementare, gemeinsame Brennmaterial der Zellen zu betrachten ist".

More or less the same situation is met with in the higher plants, in which however methylglyoxal, under anaerobic conditions, is converted chiefly in the same direction as in alcoholic fermentation.

Although in this group of organisms the affinity for hydrogen is already reduced so far that fermentative dissimilation under anaerobic conditions is very noticeable, the changes brought about do not quantitatively provide for the need of energy, which need is normally met with by the larger energetic effect of the transference of hydrogen to oxygen.

III. Organisms which cause alcoholic fermentation.

Examples: alcohol yeasts, moulds such as *Mucor racemosus.* The affinity for hydrogen of these organisms is again smaller, so that all the methylglyoxal can be dehydrogenated to pyruvic acid with relatively weaker hydrogen acceptors. The pyruvic acid produced then undergoes an intramolecular change into carbonic acid and acetaldehyde and the latter then acts further as a hydrogen acceptor in the process of the dehydrogenation of methylglyoxal [2]).

In all the groups discussed below, the affinity for hydrogen is too small to make a dehydrogenation of methylglyoxal to pyruvic acid possible with the relatively weak acceptors formed by the splitting up of the sugar. In the place of this change an intramolecular rearrangement takes place in which methylglyoxal is converted into formic acid and acetaldehyde. Along with this there always remains the possibility of the conversion of methylglyoxal into lactic acid. Both intramolecular dehydrogenations and hydrogenations are, because of reasons given previously, to a large extent insensitive to a decrease in the hydrogen affinity of the protoplasm.

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[1]) The fact that glycogen is converted into lactic acid by muscular contraction, and that this acid again disappears on the restoration of the oxygen supply, (see for example O. MEYERHOF, Die Energieumwandlungen im Muskel. Die Naturwissenschaften, vol. 12., p. 181, 1924) may not be considered as a proof of the idea — as many others including MEYERHOF are inclined to do — that also in the „Ruheatmung" i.e. under conditions of more complete aeration, lactic acid will be produced intermediately from glycogen. On the contrary under these conditions, in all probability, direct dehydrogenation with oxygen as the acceptor will occur for the greater part with the methylglyoxal or with one of the other preceding intermediate products in the formation of lactic acid under anaerobic conditions.

[2]) Meanwhile, as long as acetaldehyde is not yet formed, this view requires an introductory acceptor. Free oxygen will occur as such in most cases. Herein we see an explanation of the fact that yeast — contrary to the organisms treated below — is unable to lead a perfectly anaerobic existence, a feature, which is always taken into account in all fermentation industries, as appears from the preliminary aeration of the mash before fermentation.

IV. The bacteria of the colon-group.

The hydrogen affinity is again smaller than in group III and decreases in the order of the three sub-groups considered.

a. Sub-group of *B. typhosum*. Lactic acid, formic acid and acetaldehyde are formed in the way indicated above. The hydrogen affinity is too large, however, to allow of the formic acid being decomposed catalytically without an acceptor. The acetaldehyde is not suitable for this purpose, because it itself undergoes a powerful dehydrogenation, in which hydrogen is transferred to a second molecule, which leads to the formation of alcohol and acetic acid.

b. Sub-group of *B. coli*. In many respects the situation here is the same; only the somewhat smaller affinity for hydrogen makes the catalytic decomposition of formic acid into carbon dioxide and free hydrogen possible. Besides the acetaldehyde is dehydrogenated to a smaller extent, so that this substance can act more or less as a hydrogen acceptor in the dehydrogenation of formic acid. Also the dehydrogenation of acetic to succinic acid occurs to some extent.

c. Sub-group of *B. aerogenes*. The formation of lactic acid is here pushed into the background, which doubtless depends on the effective way in which the acetaldehyde disappears from the fermentation medium. This is a consequence of a still smaller affinity for hydrogen, which certainly brings along with it a less rapid dehydrogenation to acetic acid, but which is just the optimum for the incomplete dehydrogenation of the acetaldehyde, which leads to the formation of acetylmethylcarbinol. Both this carbinol and a portion of the acetaldehyde then act as acceptors for the more activated hydrogen formed in the catalytic decomposition of formic acid, which situation leads to the formation of 2 : 3 butylene glycol and ethyl alcohol.

V. The group of true lactic acid bacteria.

The affinity for hydrogen is again smaller than with the organisms of the foregoing group. While in the previous groups the hydrogen affinity was always so large that the corresponding oxygen affinity, although increasing from group to group, was of no account as regards the activation of hydrogen, the hydrogen affinity in the true lactic acid bacteria is so much smaller that in this case the oxygen affinity is also of importance for the activation of hydrogen. We consider that a clear indication of this may be seen in the fact, that with this group we meet for the first time with organisms which, contrary to all¹) organisms belonging to the previous groups, lack the power of bringing about the catalytic decomposition of hydrogen peroxide into water and free oxygen. This decomposition of hydrogen peroxide is, as WIELAND also remarks, undoubtedly due to a catalytic transference of hydrogen from one molecule to a second molecule. While now this investigator similarly accepts the general opinion, that the reaction in question proceeds under the influence of an independent enzyme: catalase, we must point out here that there is every reason for seeing in the reaction in question only a special manifestation of the general agent bringing about dissimilation. With the so-called catalase-negative organisms the catalytic decomposition of hydrogen peroxide will not take place for the simple reason that in this case the oxygen of the hydrogen peroxide remains fixed on the protoplasm. That the protoplasm in these organisms does indeed possess a noticeable affinity for oxygen, appears conclusively from the fact that all these organisms are characterised by a smaller or greater sensitivity towards free oxygen, which sensitivity in catalase-positive organisms is entirely lacking.

a. Sub-group of the heterofermentative lactic acid bacteria. The considerably decreased hydrogen affinity on the one hand and the relatively small oxygen affinity on the other hand, cause even easily dehydrogenated compounds as formic acid and acetaldehyde to be dislocated to only a small degree. This appears from the fact that free hydrogen is scarcely if at all met with among the dissimilation products and that the hydrogen from the compounds mentioned above is only transferred to acceptors. In the fermentation of glucose acetaldehyde functions especially as acceptor, while in the fermentation of laevulose this substrate itself is a good acceptor. Without doubt this depends on the activation of the laevulose caused by the noticeable oxygen affinity. The small power of dehydrogenation leads further to the pronounced occurrence of lactic acid formation, because the hydrogen of the methylglyoxal is insufficiently activated to bring about the rapid fission into formic acid and acetaldehyde.

b. Sub-group of the homofermentative lactic acid bacteria. In this group the dehydrogenation powers are still smaller, so that here practically only lactic acid is formed.

*VI. The group of propionic acid bacteria.*²)

The hydrogen affinity is again smaller than in the previous group and

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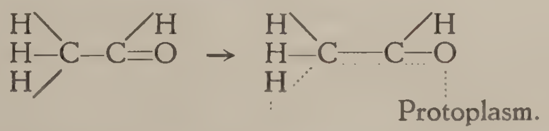
¹) After the above had been printed a species of acetic acid bacteria was isolated which so far appears to be unable to bring about the catalytic decomposition of hydrogen peroxide. Also in the meantime a paper by KNORR [Münchener medizin. Wochenschrift p. 1381, (1923)] reached us, according to which the "echte Ruhrbazillen" which are generally assigned to the *Colon*group, are quite catalase negative. On account of this a closer investigation will be instituted on the exceptions of a rule which appears to hold in hundreds of cases.

²) It must be stated that the placing of the propionic acid bacteria between our groups

consequently the oxygen affinity becomes more pronounced. On the one side this again leads to a somewhat increased dehydrogenating power which among many things is evident from the reoccurrence of the dehydrogenation of acetic acid to succinic acid. On the other hand the oxygen affinity gives rise to a noticeably more powerful acceptor activation, even to such a degree that lactic acid functions as an acceptor and is converted into propionic acid.

VII. The group of butyl alcohol and butyric acid bacteria.

a. Sub-group of butyl alcohol bacteria. The hydrogen affinity has now become so small that it has no longer any significance for hydrogen activation. Meanwhile the dehydrogenating action has again become considerably greater on account of the considerably increased oxygen affinity, which also brings along with it a powerful activation of the acceptor. The considerable affinity for oxygen shows itself very strikingly in the great sensitivity towards free oxygen, small quantities of which, as a rule, cause the death of the organism. The particular nature of the hydrogen activation caused by an affinity for oxygen appears from the fact that both in acetaldehyde and in acetic acid it is notably a hydrogen atom from the CH_3-group which is especially activated. This leads to the condensations previously mentioned. The schematic representation below illustrates this for acetaldehyde:



The particularly powerful acceptor activation is evident from the power of reducing products such as butyric and propionic acids, which are only reduced with great difficulty in the ordinary ways.

b. Sub-group of butyric acid bacteria. This sub-group differs from the foregoing only because the oxygen affinity is somewhat greater, which leads to a still greater sensitivity towards oxygen. Consequently also the hydrogen activation is again somewhat greater. The reason, that practically all transference of hydrogen on acids as acceptor remains in abeyance, is the greater acid-sensitivity, which causes the organisms to die off before the concentration of the acceptors is sufficiently high to cause any appreciable transference of hydrogen. These reasons combined lead to the result that only carbon dioxide, hydrogen, acetic acid and butyric acid occur as chief dissimilation products.

V and VII is at first quite speculative and is based only on the incomplete data which can be found regarding this group of bacteria in literature. If the observation of SHERMAN [Journal of Bacteriology Vol. 6, p. 379, (1921)], according to which the propionic acid bacteria he examined showed a strong catalase reaction, is confirmed, a revision of this grouping will be necessary.

§ 5. *Final considerations.*

While in the previous section we have limited ourselves to showing how by the help of the theory of activation and the catalytic transference of hydrogen, an insight may be obtained into the various dissimilation processes in which a sugar functions as substrate, it may be pointed out that this is equally the case for all other dissimilation processes. In this connexion we mention only the dissimilation of denitrifying, sulphate reducing, methane producing and amino acid fermenting microbes.

A logical consequence of our theory is that it is no longer necessary to have recourse to the assumption of a large number of separate enzymes to explain the partial reactions of the dissimilation process. In the light of the foregoing discussion it will be obvious that the changes which are ascribed to separate enzymes such as catalase [1]), reductase, zymase, lactozymase, alcoholoxidase, carboxylase, carboligase, glyoxalase, aldehydomutase, SCHARDINGER's enzyme etc., are actually only manifestations of a definite degree of affinity of the protoplasm for hydrogen. The question as to how far one will think of the affinity of protoplasm itself for hydrogen or of the action of a single hydrogen transferring enzyme, has no significance here.

Finally let it be expressly stated that while, in the previous sections, we have represented the affinity for hydrogen of the protoplasm of a definite organism as constant, this affinity in reality varies to a certain extent with the hydrogen ion concentration in the protoplasm. From a number of concordant examples we are of the opinion that we may conclude, that within the region of hydrogen ion concentrations, which are harmless for the organism, a decrease of the concentration brings about a decrease in the affinity of the protoplasm for hydrogen. In connexion with the fact that every dissimilation of sugar practically always goes parallel with the formation of acid, and on the other hand every dissimilation of the hydrolytic decomposition products of proteins gives rise to ammonia, organisms, which are more adapted to action on carbohydrates, have a region of development situated at higher hydrogen ion concentrations than organisms more suited for acting on protein decomposition products. From all this we may conclude, that the dissimilation of every living cell is determined only by the limits of the allowable hydrogen ion concentrations on the one hand and the affinity of the protoplasm for hydrogen within these limits on the other.

We intend to return to the above considerations elsewhere in greater detail.

Delft, February 1925.

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[1]) Here we mean only the insoluble catalase, the so called α-catalase of LÖW.

Ophthalmology. — *"On Enlargement of the "Optic Foramen"*. By Prof. J. VAN DER HOEVE.

(Communicated at the meeting of April 25, 1925).

In normal persons the size of the optic foramen shows only very little individual variations. WHITE's anatomic research showed that the diameters of the canalis opticus ranged from 4—6.5 m.m. GOALWIN's averages varied from 4.26 to 4.5 m.m.

My own observations are chiefly based on röntgenograms of the foramen.

The method of photographing the foramen opticum by Röntgen rays has first been suggested by RHESE. This author, who tried to find and actually did find in his method an excellent means to photograph the the accessory nasal cavities, did not realise himself the significance of his invention. It was A. DE KLEYN who pointed to the great use of this procedure for ophthalmology. In collaboration with STENVERS he slightly modified RHESE's method, so that the optic foramen and the fissura orbitalis superior could be observed more distinctly and these authors showed that in cases of accident: fractures, fissures and later on callus formation could be found in the bony environment of these holes.

Since the first announcement of their experience, nine years ago, I had Röntgen photos taken of the foramen opticum as often as opportunity offered. From the results of my rather extensive experience I learnt that at a distance of 75 c.m. from the Röntgentube to the photographic plate the diameter of the foramen varied from 4—6 m.m. A foramen of 6 m.m. looks a bit suspicious, one of more than 6 m.m. I consider to be decidedly too large.

The form of the foramen on the röntgenogram is perfectly circular, oval, or slightly angular. GOALWIN considers them as quadrants.

What we really see on the photographic plate, is not the foramen opticum, but a projection of the lumen of the canalis opticus. Obviously a wrong position of the patient's head may give a projection that is too small but not one that is too large. For this reason greater precaution should be exercised in diagnosing too small a foramen than an abnormally dilated one. If an abnormally large image is found on the röntgenogram, the foramen is certainly too large.

Of late I have given special attention to the possibility of an enlargement of the optic foramen, being convinced that it might occur just as well as an enlargement of the meatus auditivus internus sometimes will occur. Like the optic foramen the meatus is also an opening encircled on all sides by bone which affords a passage for a nerve; tumours of the auditory nerve or its environment may enlarge this hole. The study of this enlargement on the röntgenogram is of great significance for the identification of these tumours.

The enlargement of the meatus auditivus internus is occasionally observed in RECKLINGHAUSEN's disease, in which pontile tumours (occurring most often bilaterally in this disease) may occasion deafness and dilatation of the inner auditory canal.

Now considering that this discase may also be attended with blindness or weak eyesight caused by atrophy of the optic nerve, I suspected that this blindness in some case might be attributed to tumours simular to those occurring along the auditory nerve or to diffuse neurofibromatosis of the optic nerve itself. Both processes might possibly engender dilatation of the optic nerve canal to such an extent, that it might be imaged on the röntgenogram.

The first patient that I examined to ascertain this, was blind at the right eye and had a markedly reduced visual acuity at the left eye. The application of Röntgen rays proved that the right optic foramen was far wider than normal, while the right optic foramen was much wider still. (See fig. *b*[1] and *b*[2] as compared with the normal optic foramen *a*).

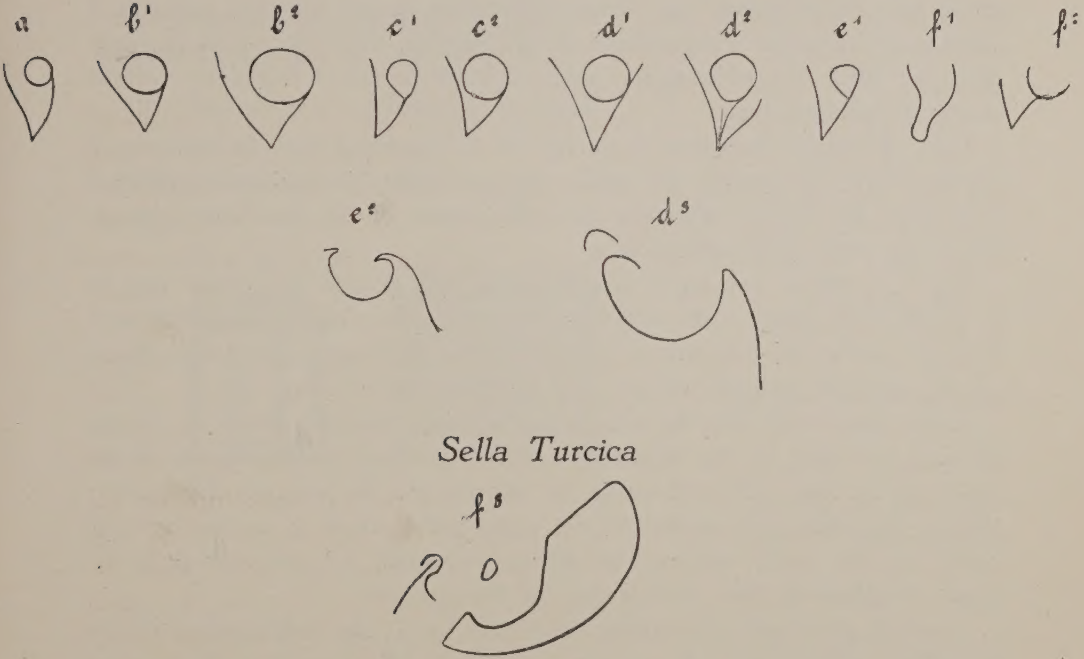
An acute deterioration of the eyesight necessitated operation. It was performed by Prof. ZAAYER. We then observed that there were no definitely marked tumors in the foramen opticum, but that the two optic nerves were much thicker than normal, which was presumably owing to neurofibromatosis.

Prof. ZAAYER removed the roof of the optic canal and slit the dura mater, so that the optic nerve was relieved of pressure. The result was very satisfactory: visual acuity and field of vision improved considerably, and at the present time, two years after the operation, patient still enjoys a fairly good eyesight.

This, then, went to show that a long-continued swelling of the optic nerve can induce a marked widening of the foramina.

In another patient the widening was generated by a tumour growing out from the orbit towards the cranial cavity. When two years old this patient had been brought to me for glioma retinae of the right eye. At the time the parents objected to having the eye enucleated immediately. After ten months the child was brought to me again in a sorry plight; the eye was blind, excessively dilated, while it gave an impression as if there was tumourous mass also in the orbit. Being convinced that the optic nerve was affected, I had photos taken of the foramina. It appeared now that the diameter of the foramen at the diseased side equalled about twice that at the healthy side (fig. c[1] and c[2]). Besides this a small portion of the wall of the enlarged foramen opticum had been corroded.

After the whole orbit had been evacuated, it appeared that the optic nerve had thickened considerably, so that the area of the section equalled about four times the normal surface. This goes to show that in young individuals a thickening of the optic nerve, which has originated from a tumourous growth, can give rise to enormous dilatation of the optic foramen.



Röntgen pictures of the Optic Foramen.

Sella Turcica

a. normal; *b.* enlargement by neurofibromatosis diffusa; c¹ normal and c² diseased side in glioma retinae. *d.* dilatations in hydrocephalus. e. normal condition in hydrocephalus; *f.* dilatation and destruction in glioma of the chiasm, all on the same scale.

A third case tended to show that also tumours growing out from the cranial cavity towards the orbit can expand and affect the optic foramen. A female patient was brought to me from the neurological ward, because she had lost the visual acuity of both eyes in a short time. The left eye was still slightly sensible to light.

From the ophthalmoscopic picture I learnt that we had to do here with primary atrophy of the optic nerve as well as with choked disk. This led me to make the presumptive diagnosis glioma of the chiasm and the optic nerves, as recently described by MARTIN and CUSHING. In this case I expected a change of the sella turcica and incidentally also of the foramen opticum. As will be seen the röntgenogram really revealed a marked dilatation and an almost complete destruction of the sella turcica (fig. *f*³), while on the side of the eye that had still retained some perceptive power, the foramen opticum had merged into the fissura orbitalis superior (fig. *f*¹), and at the blind eye only the lower part of the wall of the enlarged optic foramen was still present (fig. f^2). The line of the base of the skull was almost completely destroyed, which could also be seen on stereoscopic röntgenograms. During the printing of this article I observed a quite similar case in a less advanced stade.

Since it has been proved by the above that tumours, developed along the optic nerve, can induce dilatation of the foramen opticum, I suspected that mere overpressure in the fluid of the cranial cavity might generate also this dilatation; with a view to this I examined various cases of hydrocephalus.

One of them concerned a patient of 10 years of age. In this case I observed the dilatation, the sella turcica being considerably enlarged (d^3). Figs. d^1 and d^2 illustrate the enlargement of the foramen opticum, while the wall remained smooth.

Figs. e^1 and e^2 present a foramen and sella turcica of normal size in a child of 8 years, also with hydrocephalus. Further investigation will perhaps settle the question in what cases of hydrocephalus enlargement of the foramen opticum occurs and in what cases it does not.

It has been seen that the expansion is easily brought about in young patients. So long as the causative agent is confined to the sheaths of the optic nerve, the wall will retain its smoothness; as soon as the tumour affects also the environment of the optic nerve, there is a chance of the walls of the optic nerve-canal being corroded, as was shown in the cases of glioma retinae and glioma of the chiasm.

Various problems still remain unsolved, i.a. if the enlargement of the foramen opticum will also occur with other affections that cause overpressure in the skull of young patients, e.g. microcephalus through premature closure of the cranial sutures.